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CLASSIFICATION OF BITUMENS IN ASPHALT TECHNOLOGY BY CERTAIN RHEOLOGICAL PROPERTIES

PART I

THE USE OF VISCOSITY AND CONSISTENCY TESTS IN THE CLASSIFICATION OF ASPHALTIC BITUMENS: A CRITICAL SURVEY OF EXISTING KNOWLEDGE

By S. L. NEPPE (Fellow)

SYNOPSIS

A critical survey of the literature on bitumen viscosity and consistency measurement has been made as a necessary preliminary to the author's own experimental work and derivations which are reported in subsequent parts of this work.

Various aspects of the standard ring and ball softening point, penetration, and ductility tests and their inter-relationships are also discussed.

Different graphical representation methods used by other investigators in relating viscosity with temperature are examined and improvements suggested to a number of relationships. The present position regarding the classification of asphaltic bitumens is summarized together with a discussion on the comparative utility values of various temperature-susceptibility factors and penetration indices.

Certain anomalies in the present system of standard penetration values are pointed out, and a more rational conception of "true penetrations" is advocated by the author as a logical development to the work of Pendleton, which takes into account the shape and dimensions of the penetrometer needle.

BITUMEN CONSISTENCY TESTS

WITH the development of the asphalt industry, several arbitrary conventional test methods for measuring the consistency of bitumens have been evolved, some of which have gained sufficient recognition to become standard procedures for most routine purposes.

Of these, the following, excluding actual viscosity tests, are the most common. The working details of the various methods are well known, and can be found by reference to the relevant literature.

Type of test	Test designation or reference
1. Softening Point:	
(*a*) Ring and Ball (R & B)	IP 58. ASTM D36.
(*b*) Kraemer–Sarnow (K & S)	STPTC PT 3.
(*c*) Cube in Water	ASTM D61.
(*d*) Ubbelohde Drop Point	Ref. 107
(*e*) Hoepfner-Metzger Solidifying Point	Ref. 34
2. Penetration	IP 49. ASTM D5
3. Ductility	IP 32. ASTM D113
4. Float Test	ASTM D139
5. Twisting Point	STPTC PT 2.
6. Fraas Brittle Point	DIN 1955–A7

Tests 1(*a*), 2, and 3 are by far the most extensively employed.

The penetration test is perhaps the most important for readily measuring consistency, and is the basis upon which most solid and semi-solid bitumens are classified for trade purposes.

The float test is used mainly in cases where a material is too soft for a penetration test, and either too viscous at the temperature desired for test or too small in quantity for a viscosity test.

Tests 5 and 6 are generally reserved for special purposes, particularly in work on tars. Rigden [79] has shown that the Fraas brittle point defines the temperature at which the viscosity is approximately 5×10^9 poises.

Other useful arbitrary consistency tests devised to measure "relative tendency to flow" include the thin film (3 to 5 mm) test of Pfeiffer and van Doormaal [69] and the L-mould test recommended by the Institute of Petroleum.[120]

In view of their important role in the present work, the significance and merits of the softening point, penetration, and ductility tests are discussed separately later.

It should be realized that although all the foregoing practical tests have their own particular significance, in each case they simply give an arbitrary measurement of some physical property. Individually, these tests do not indicate the service characteristics of a bitumen or its suitability for a particular commercial application; nor does any single test by itself provide a direct measure of all the rheological properties of a bitumen, since one isolated test cannot clearly bring to light any special properties which the bitumen may possess to a high degree, such as plasticity, elasticity, or thixotropy. When, however, two or more of these tests are carried out on the same sample, the results can be considered in relation to each other, and much valuable information may be derived. As will be seen later, several classifications of bitumens have been attempted on such premises both by previous investigators and by the present author.

It is generally recognized that all these empirical tests are fundamentally measurements of viscosity, but other properties of the bitumen such as density, surface tension, adhesiveness, etc., have an effect on the final result, the relative influence of each, however, being an uncertain quantity. Each method characterizes the phenomenon of flow in its own way, but does not differentiate between the different possible kinds of deformation.

As a consequence of the foregoing, the trend of fundamental research work on the rheological properties of bitumen has more recently been in the direction of absolute viscosity measurements over a range of temperatures. The present investigator has nevertheless deliberately concentrated on relating certain conventional empirical tests used widely in the asphalt industry in order to evaluate the utilitarian qualities of asphaltic materials in a rapid and reliable manner. The experimental and derivative data on this subject are dealt with fully in a subsequent paper. (See Part II of this work.)

Other viscosity-measuring equipment required to complete the picture of temperature susceptibility over a wide range of temperatures has also

been used in these researches, and a section is accordingly devoted to a review of viscosity measurement.

The Measurement of Bitumen Viscosity

It is preferable, if possible, to make determinations to cover the whole range of viscosities which may be encountered in practice, *i.e.*, from about 1 to 5 poises, at which asphalts are sufficiently fluid to work easily in paving plant,[85] up to as much as 10^{10} or even 10^{13} poises, which may characterize hard, blown bitumens at low temperatures. However, it is quite unnecessary to carry out individual determinations at regular intervals throughout this range provided a suitable mathematical or graphical relationship has been definitely established between viscosity and temperature over the range under consideration.

Thus, tests may be made at two, three, or more temperatures as required, and the viscosities at other temperatures may be determined by inter- or extra-polation as necessary.

Temperatures most commonly employed in routine practice are usually selected from 60°, 77°, 100°, 122°, 140°, 158°, 176°, 200°, 225°, and 275° F. It will be noted that temperatures as low as 32° F are not included in this list. This is due to experimental difficulties consequent upon the very high viscosities of bitumen at such low temperatures requiring very long periods of testing with an accompanying sacrifice of accuracy. Viscosity determinations at 275° F are generally chosen, because it is usually found that data can readily be obtained at this temperature for the most common grades of bitumen, viz., those varying from 200 penetration down to 25 penetration at 77° F. While higher temperatures may be employed, differences between bitumens from various sources become less marked as the temperature is increased, and, for softer materials, the limits of accuracy of the viscometer used must be taken into consideration.

Great practical difficulties are involved in developing a single instrument to evaluate rapidly and accurately all types and consistencies of asphalts over the wide temperature ranges desired. Consequently, it has been found convenient in asphalt-technology practice to utilize a number of different types of viscometers, each with its own approximate confined range.

The more important classes of these instruments may be classified under the following general group headings :—

(*a*) Flow from an orifice.
(*b*) Capillary tube viscometers.
(*c*) Coaxial cylinder viscometers.
(*d*) Falling sphere viscometers.
(*e*) Rotating cylinder viscometers.
(*f*) Torsion type viscometers.
(*g*) Flow along inclined plane.
(*h*) Miscellaneous.

A considerable number of forms and modifications of these viscometers have been used by different workers in their investigations on bitumen viscosity, and a comprehensive list of such instruments from data obtained

TABLE I

Instruments in Use as Bitumen Viscometers

Type or description of viscometer	Method	Approx temperature range, °F	Approx viscosity range, poises	Typical references
1. Rod	Saal		10^7–10^{13}	83
2. Penetrometer	ASTM D5		10^4–10^{12}	55, 67, 94, 99, present work
3. Disk	Obermayer		10^7–10^{12}	57
4. Metro plastimeter	Evans–Pickard	60–90	10^8–10^{10}	22, 23, 71
5. Falling coaxial cylinder	Pochettino	32–100	10^7–10^{10}	24, 25, 44, 45, 54, 73, 83, 98, 104
6. Alternating stress	Bingham–Stephens	60–95	10^5–10^8	8, 72, 98, 101, 103, 104
7. Conicylindrical rotation	Couette	77–(150)	0·01 –10^5	11, 14, 45, 46, 63, 83, 98, 106
8. Twisting point	Frankland Taylor		10^3–4×10^7	10, 11, 42
9. Capillary tube	Modified Bingham–Murray	110–270	10–10^6	61, 72, 83, 98, 101, 104
10. Capillary tube	Modified Ostwald	60–140	Up to 10^6	18, 45, 61
11. Rotating cylinder	Csagoly		1–10^6	15, 16, 102
12. Plastometer	Bingham–Murray	(212)–270	5–10^5	7, 72, 98
13. Sinker	Saal		0·1–10^5	83
14. Rising-column capillary tube	Rhodes–Volkmann–Barker	110–200	60–6×10^4	26, 48, 78
15. Modified BRTA Trough	Selvey	85–195	60–10^4	86, present work
16. Rotating cylinder	Volarovich	110–212	25–$2{\cdot}1 \times 10^4$	42
17. Falling sphere	Höppler		Up to $1{\cdot}2 \times 10^4$	11, 38
18. Orifice efflux	BRTA (STPTC RT2)		80–1000	86, present work
19. Trough	Evans–Pickard	60–200	30–1000	22, 23, 71
20. Torsion	Brookfield Synchro–Lectric		0·1–1000	9, 53, 88
21. Torsion	Fuidge		Up to 100	27, 28
22. Ball and bucket	Beale–Docksey		Up to 100	5
23. Orifice efflux	Saybolt–Furol (ASTM D88)		0·5–50	98, 114
24. Orifice efflux	Redwood II (IP 70)		0·5–50	13, 83, present work
25. Orifice efflux	Engler	350–400	0·1–10	1, 110
26. Conicylindrical rotation	Stormer	325–450	0·1–20	87
27. Conicylindrical rotation	MacMichael	325–450	0·1–20	87

from divers sources is given in Table I, which shows the approximate range of these viscometers as reported in the literature. For simplicity, the various instruments have been arranged in approximate descending order of upper limit poises, and the whole range of viscosities normally encountered in practice has been covered.

In several instances the stated upper or lower limits, or both, are probably far from the true limiting values, but are useful in according information on their actual reported usage. In some cases temperature limits have also been included simply as an indication of values used in practice, but these are obviously entirely dependent on the viscosity properties of the bitumens under test. Details of construction and methods of utilization of the various instruments can be found in the original references.

Each type of apparatus has its own special characteristics of limited applicability, sensitivity, advantages, and disadvantages, and has been checked against other standards to ensure that the instruments are in fact measuring the same property and that no factors have been overlooked in a correlation of the various viscometers.

Formulæ converting measurements in empirical units directly into absolute units of viscosity have been derived for most of the instruments on the basis of the relevant theoretical principles involved, due allowance being made in each case for the special instrument constants which are dependent on the respective viscometer dimensions and on other factors. Conversion tables are readily available in the literature.

The importance of the effect of shear stress in viscosity determinations cannot be over-emphasized.

In certain torsion viscometers, for example, the drag of the liquid on a spindle rotating at a constant speed is transmitted in tension through a calibrated spiral spring and recorded on a dial. These instruments are equipped with simple gear-changing mechanisms which enable the behaviour of bitumen to be studied at definite predetermined rates of shear, which can be applied, as required, by small adjustments to the apparatus.

The examination of materials under such variable rates of shear provides a sure means of identifying non-Newtonian bitumens and of establishing the presence and extent of thixotropic, dilatant, and other rheological properties.

Again, the design of conicylindrical viscometers is such that shearing stresses can be controlled, as desired, over a wide range covering 626 to 105,000 dynes/sq. cm.[45, 46]

Other instruments, on the other hand, are more limited in their applicability. The falling coaxial cylinder viscometer, for example, has a range of 1400 to 7000 dynes/sq. cm.[24]

In efflux-type viscometers the rate of shear is very low and cannot be varied. Such instruments, whilst disclosing the kinematic viscosity of the liquid under test in an almost quiescent state, are not adapted for the detection of anomalous flow characteristics simply because they indicate only one period of time required for the passage of a fixed quantity of liquid through an orifice—*e.g.*, Redwood, Saybolt, or Engler viscometers—or through a capillary. Thus, viscosities obtained with a modified Ostwald capillary tube are determined under a constant shearing stress of about 3000 dynes/sq. cm.[45, 46]

Pfeiffer and van Doormaal report the following approximate values of shearing stress applicable to some other well-known tests :—

	Dynes/sq. cm.
Thin film flow test	100–500
Redwood II viscometer	200
Sinker viscometer	10^3
R & B Softening Point	10^3
Penetration 300	10^5
Penetration 30	10^6
Penetration 3	10^7

According to Bingham and Stephens [8] the measurements in extreme cases are sometimes not even qualitatively exact, since with one viscometer employing a certain shearing stress, a given bitumen may appear to be stiffer than another, yet when an instrument is used in which a different shearing stress is employed, the second bitumen may conceivably be stiffer than the first.

Pfeiffer and van Doormaal,[69] however, point out that in general the shearing stresses applied must vary almost proportionately to the viscosity, since asphaltic bitumens must comply with the relation :—

$$\text{Deformation Velocity} = \text{Shearing stress}/\text{Viscosity},$$

and all viscosity determinations, to be applicable in practice, have necessarily to be carried out at deformation rates of approximately the same magnitude.

In their opinion the rheological properties of bitumens at very low temperatures should be studied under high shearing stresses, since the deformations to which these products are subjected in their technical application at low temperatures bring about very great shearing stresses in the material. Conversely, viscosities at high temperatures should be measured at low shearing stresses.

Lee, Warren, and Waters [46] have shown that the change in viscosity with change in temperature is much greater under small shearing stresses than under large. The difference in susceptibility is, however, greatly reduced with more fluid bitumens where the viscosity is less than 10^4 poises.

In the present investigations (see Part II and subsequent papers of this series) considerable use has been made of the penetrometer in studies on consistency–temperature relationships, particularly at low temperatures. Two other instruments mentioned in Table I have also been used, namely the Redwood II for high-temperature work and the modified BRTA-trough viscometer for intermediate temperatures.

Graphical Representation Methods for the Viscosity–Temperature Relationship

The necessity for suitable methods of expressing temperature-susceptibility characteristics quantitatively is evident from the foregoing discussion, and various factors, mostly empirical in nature, have been proposed from time to time for comparing different bitumens over limited ranges of temperature. These factors have in general been based upon consistency and viscosity measurements made according to the methods already indicated, and will be discussed later.

The writer has found that viscosity–temperature relationships of asphaltic bitumens and coal-tar pitches have in the past been presented in as many as six different graphical ways, mainly with a view to obtaining some straight-line relation.

These are :—

(*a*) Log viscosity *vs* ordinary temperature (in ° F or ° C)
(*b*) Log viscosity *vs* log ordinary temperature.
(*c*) Log viscosity *vs* log absolute temperature.
(*d*) Log viscosity *vs* reciprocal of absolute temperature.
(*e*) Log viscosity *vs* reciprocal of square of absolute temperature.
(*f*) Log log viscosity *vs* log absolute temperature.

Log Viscosity vs *Ordinary Temperature*

If a straight-line relationship holds, the general equation in this case is

$$\log \eta = k - mt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

where η is the absolute viscosity in poises,
t is the temperature of ° F or ° C,
k and m are constants.

Saal [81] has illustrated that, over a full range of 150° C, a smooth curve is obtained which shows no break in the relation between temperature and viscosity. This indicates that there is no sudden change in the physical properties, but a gradual transition from a condition approximating true solution to a distinctly colloidal state. This is also in accord with the notion discussed elsewhere [64] that when a bitumen cools, the asphaltenes gradually separate from solution in the oily constituents and become associated, giving rise to a stable system, the colloidal properties of which become more pronounced as the temperature is lowered farther and farther.

Though no break was obtained in the particular viscosity–temperature curve examined by Saal, this does not preclude the possibility of sudden changes being noted in other consistency–temperature curves with other bitumens of different physical characteristics, without affecting the colloidal theory of asphalt in any way. In fact, several instances of sharp breaks have been noted by the present investigator, and will be pointed out in due course in the experimental section of this work (see Part II, *et seq*).

Though the curve for log viscosity–temperature as a whole is far from being perfectly linear, Traxler and his co-workers [85, 98, 103] consider that the portion between 15° and 40° C is sufficiently a straight line within limits of experimental error, and the same type of equation also holds for narrow ranges at high temperatures.

On this assumption, they have taken equation (I) as a basis for evaluating the susceptibility of asphalts to temperature changes in terms of the percentage decrease in viscosity (in poises) for a 1° Celsius rise in temperature. Thus :—

$$\text{Asphalt Viscosity Index (A.V.I.)} = 100\left[\left(\frac{\eta_{ia}}{\eta_{ib}}\right)^{\frac{1}{t_a - t_b}} - 1\right]. \quad \text{(Factor A)}$$

where η_{ia} and η_{ib} are the absolute viscosities at ordinary temperatures t_a and t_b respectively.

This relationship looks fairly formidable, but is only a natural mathematical development based on the slope of a linear temperature–viscosity relation for the temperatures under consideration, and is in accordance with the meaning of the term "susceptibility" as change of viscosity with temperature.

The value of this susceptibility factor as an index of bitumen quality together with indices suggested by several other workers has been critically examined by a number of investigators (see later), but it is significant that the originators themselves emphasize the limited applicability of their index to fixed narrow temperature ranges by quoting a variation in A.V.I. for one particular asphalt from 20·5 at low service temperatures to 4·4 at high processing temperatures.

Log Viscosity vs *Log Ordinary Temperature*

The general equation for a straight-line relationship according to this method is

$$\log \eta = k - n \log t \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(II)}$$

or

$$\eta = at^{-n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(IIA)}$$

where n, k, and a are constants with $k = \log a$.

This type of curve has been used by Evans and Pickard,[22] Pickard,[71] Allen and Gibson,[2] Mitchell, Lee, and associates,[45, 46, 62] and by Lewis and Hillman.[50] In this case the resultant plot also has a slight curvature, but only over really wide ranges of temperature, and the equation is without doubt reasonably applicable for narrower ranges. For example, it has been shown [46] that the equation can be applied for bituminous binders of viscosity up to 10^7 poises over a fair temperature range of 68° to 194° F, the viscosities being measured at the same shearing stress throughout the range.

It is worth noting the observations of Mitchell and Lee [62] on the change in structure of low aromatic tar at a temperature of about 32° F. They found that when log viscosity was plotted against log temperature, instead of the straight-line relationship usually obtained, two straight lines inclined to each other at a very small angle were obtained, the junction being in the region of 32° F.

The slope of the straight line obtained by this log η — log t plot, or the coefficient n in equation (II), has been termed the "logarithmic temperature coefficient" by Mitchell and Lee, and provides a criterion for distinguishing between the relative susceptibilities of different bitumens.

$$\text{Thus, L.T.C.} = n = \log \eta_1 - \log \eta_2 / \log t_2 - \log t_1 \quad . \quad . \quad \text{(Factor B)}$$

Log Viscosity vs *Log Absolute Temperature*

This method differs from the preceding one in that the log of the absolute temperature is used as the abscissa instead of log of the ordinary temperature. From a scientific point of view it is decidedly more rational, as it gives a relation which is absolute in basis.

In this case, the fundamental linear equation is :—

$$\log \eta = k - n \log T \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(III)}$$

or

$$\log \eta = aT^{-n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(IIIA)}$$

where, in this case,

T is temperature in ° F absolute or ° C absolute;
n, k, and a are constants with $k = \log a$.

This method has been used by Lang and Thomas,[44] who suggested a Viscosity Index very similar to that of Mitchell and Lee, but has been limited intentionally to a low-temperature range from 33° to 77° F. Thus :—

$$\text{V.I.} = \frac{\text{Log Visc at 33° F} - \text{Log Visc at 77° F}}{\text{Log } T_{77} - \text{Log } T_{33}} \quad \text{(Factor C)}$$

where T_{77} and T_{33} are absolute temperatures.

The denominator is obviously a constant, and, since the index is arbitrary, the present author considers that it can be simplified considerably to include only the numerator, thus :—

$$\text{V.I.} = \text{Log Visc at 33° F} - \text{Log Visc at 77° F} . \quad \text{(Factor N C)} *$$

Log Viscosity vs *Reciprocal of Absolute Temperature*

This is based on Andrade's fundamental viscosity–temperature equation for pure liquids [3] viz. :—

$$\eta = Ae^{-B/T}$$

or

$$\log \eta = \log A - B/T \log e$$

where A and B are constants.

In such a case, therefore, a straight line should be obtained if the logarithm of the viscosity is plotted against the reciprocal of the absolute temperature. This is, however, not quite possible theoretically, since in practice the values of A and B in the equation are not absolutely constant, but, according to Hardiman and Nissan,[31] are themselves somewhat affected by changes in temperature.

The equation has been examined by Lewis and Halstead,[48] who show graphically, over the range 45° to 85° C, that this form of relationship is also not quite correct, owing to the definite curvature obtained on plotting the results. They remark, however, on the possibility that the viscosities obtained with their instrument at or near softening-point temperatures are higher than the true viscosities because of instrument limitations. Consequently, the curvatures in their graph may be rather exaggerated.

Lewis and Halstead have evinced particular interest in these curves because they take into account the physical characteristics of the asphalts, and no empirical constants have been introduced. They are of the opinion that such curves can be very valuable in a study of the deviations of asphalts from true liquids.

Log Viscosity vs *Reciprocal of Square of Absolute Temperature*

The equation to the straight-line in this case is :—

$$\log \eta = b - m/T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(IV)}$$

This method of plotting the viscosity–temperature relationship was first

* The use of the letter N in front of the symbol C in this instance is to indicate the present writer's modification of the original equation. A similar system has also been adopted in other parts of this work, where applicable.

used by Umstatter,[109] who obtained straight lines over the range 25° to 50° C. The equation was checked by Traxler and Schweyer,[103] who found that a good approximation to a straight line was obtained when the graphical method was applied to data for a number of different kinds of bitumen over a temperature range of 15° to 50° C. The relation was also shown to hold fairly well over the range 80° to 200° C, but for any bitumen the value of the slope m for the higher-temperature range is different from that for the lower. Thus, in the region of 50° to 80° C lines plotted for asphalts according to this method meet at an angle, indicating radical changes in the character of the bitumens. It is significant that the softening points of the asphalts also lie between 50° and 80° C, further indicating some fundamental change in the structure of the bituminous systems. This change in structure is regarded as being responsible for the difficulties encountered in obtaining a simple expression for temperature–viscosity relationships over an extended range.

Log log Viscosity vs *Log Absolute Temperature*

The most accurate expression for graphical representation of viscosity–temperature data over the widest ranges was found by Ubbelohde and his co-workers [108] to be based on Nevitt's fundamental equation for petroleum products,[65] viz. :—

$$\log A\,(\mu + 0{\cdot}8) = KT^{-m} \quad . \quad . \quad . \quad . \quad . \quad (\text{V})$$

where μ is the kinematic viscosity in centistokes at the absolute temperature T;
A, K, and m are constants.

This form of equation has also obtained the official recognition of the American Society for Testing Materials as the basis for the construction of the tentative standard viscosity–temperature charts for liquid petroleum products (ASTM D341 — 32T).

The equation can obviously also be written in the form :—

$$\log \log A(\mu + 0{\cdot}8) = c - m \log T \quad . \quad . \quad . \quad (\text{V}_\text{A})$$

where c is a constant and equal to $\log K$.

Nevitt's equation has been verified in principle by Zichner,[116] Lewis and Halstead,[48] Finney and Wolczynski,[26] Fair and Volkmann,[24] and Saal.[80, 82] The last-mentioned showed that the viscosity correction of 0·8 should in fact be 0·95, and accordingly modified equation (V_A) to give

$$\log \log (\mu + 0{\cdot}95) = c - m \log T \quad . \quad . \quad . \quad (\text{V}_\text{B})$$

It should be appreciated that when μ is 100 centistokes (or 1 stoke) that the correction is only 0·95 centistokes (or less than 0·01 stokes). The viscosity range for asphaltic bitumen may, however, extend from over 10^{10} stokes at very low temperatures down to 1 to 5 stokes at high temperatures of about 300° to 400° F.

It follows therefore that the correction factor is generally extremely small and can usually be neglected without materially affecting the accuracy of the plotting or the viscosity value obtained by using the equation. Consequently, if the double logarithm of the viscosity is plotted against the

logarithm of the absolute temperature, a straight-line relationship should be obtained.

Fair and Volkmann [24] have used this form of equation for two typical tar pitches and have found that in each case below the softening point the temperature susceptibility is lower than it is above that temperature, indicating a break in the curve near the region of the softening point. They also point out another example where the reverse applies.

Similar observations are made by Broome,[13] who illustrates the difference in behaviour of bitumen and pitch on slow heating beyond the softening point. Bitumen is shown to increase in fluidity at a relatively slow rate, whereas a pitch of coal-tar origin becomes quite fluid at a temperature only slightly in excess of the softening point.

Zichner [116] has suggested the characterization of a binder by the temperature at which it has a definite viscosity in much the same way as the equiviscous temperature has been adopted in tar technology. He also recommends a susceptibility factor which is numerically the temperature interval necessary to increase the viscosity from 80 to 200,000 centistokes.

These values could be inter- or extra-polated from the log log viscosity *vs* log absolute temperature plot of determined data.

Nevitt and Krchma [58, 66] have shown that the slope m of the straight-line obtained by plotting Nevitt's basic equation is mathematically

$$m = \log\left[\frac{\log(\mu_1 + 0{\cdot}8)}{\log(\mu_2 + 0{\cdot}8)}\right] \Big/ \log\frac{T_1}{T_2} \quad . \quad . \quad . \quad . \quad \text{(VI)}$$

where μ_1 and μ_2 are the kinematic viscosities in centistokes at the absolute temperatures T_1 and T_2 respectively.

In order to simplify matters, these workers have suggested that their "viscosity–temperature susceptibility coefficient" (V.T.S.) be obtained by direct reference to the ASTM chart D341–32T, in which the V.T.S. is the actual slope of the straight line connecting the points obtained by plotting the asphalt viscosities on the chart.

This necessitates a slight modification to the above formula in which an extra constant has to be introduced to allow for the scales used in the chart, so that

$$\text{V.T.S.} = 0{\cdot}221 \log\left[\frac{\log(\mu_1 + 0{\cdot}8)}{\log(\mu_2 + 0{\cdot}8)}\right] \Big/ \log\frac{T_2}{T_1} \quad . \quad \text{(Factor D)}$$

This relationship—though numerically empirical on account of the convenient additional constant 0·221—is nevertheless more fundamental in nature than any of the others discussed in this section, and is applicable over all ranges of temperature.

In view of the foregoing, the present author has adopted the principle that all viscosity–temperature relationships be represented graphically on a log log viscosity *vs* log absolute temperature basis so as to ensure wider applicability. It should, however, be appreciated that, where fairly narrow temperature ranges are being considered, the simpler methods of plotting are at times probably more advantageous in that small differences are more eagerly discernible on the graphs.

The Ring-and-Ball Softening-point Test

ASTM D36; IP 58.

It has already been pointed out that none of the recognized methods normally used in physical chemistry for the determination of melting points of pure substances can be applied to bituminous materials. Arbitrary tests have therefore had to be devised.

Abraham [1] uses the term "plastic range" to denote the temperature range over which the gradual transition from solid to liquid takes place. The lower limit of this range is considered to be the solidifying point of Hoepfner and Metzger,[34] and the upper the liquefying or drop point of Ubbelohde,[107] while the two softening points obtained by the Kraemer–Sarnow (STPTC PT 3) and the ring-and-ball standard methods are intermediate between the two limiting values. The extent of the plastic range between the solidifying and liquefying points constitutes a numerical index for each particular bitumen and represents its resistance to changes of temperature. For example, a sample of asphaltic bitumen may have a plastic range of 160° F as compared with about 85° F for a coal-tar product.

Abraham has also shown that there is an approximate relationship connecting these transition points; the "degree of softness" exhibited by bitumens at the K and S and R and B values is said to occur at temperatures corresponding to 68 and 87 per cent of the plastic range respectively. Such points, therefore, are really arbitrary but nevertheless standardized temperatures at which a bitumen is considered to soften and becomes more or less fluid. The relationships between the softening points determined by different methods have also been investigated by Pickard,[71] by Ubbelohde and his collaborators,[108] and by Fuidge and Deadman.[28]

Chemically, the softening point depends upon the fluidity or viscosity of the oily constituents and rises rapidly with an increase in the proportion of asphaltenes and resins.

The ring-and-ball softening point has in general been accepted as a standard in asphalt-paving technology. Under definite prescribed test conditions it represents that temperature at which the cohesion of a bitumen is overcome sufficiently to permit a sample, confined in a brass ring of fixed dimensions and loaded with a steel ball of given size and weight, to fall through the ring. The degree of reproducibility according to the ASTM requirement is given as 1·8° F maximum difference between duplicate determinations, but the Institute of Petroleum allows greater latitude and specifies that test results should not differ from the mean by more than 1·8° F for values between 95° and 176° F, whilst outside these limits a 3·6° F mean difference is accepted. In this connexion it must be appreciated that the method of test laid down by the standardizing bodies should be rigidly followed at all times to obtain the precision required, as softening-point determinations may be radically affected by a number of factors. These have been fully examined in a recent publication by Krom,[43] who has shown that there is no advantage in mechanical stirring of the bath in accordance with IP 58. The experimental data show that stirring reduces the softening points for all bitumens by about 2·9° F as compared with no stirring under ASTM D36. The latter procedure has been

rigidly followed in the present investigations reported in subsequent papers of this series.

Various modifications to the test procedure to obtain reasonably accurate results in practice, particularly for routine control, have been suggested by Hersberger and Overbeck [32] and by Wilson.[112]

From the point of view of practical usefulness, the softening-point test offers a good basis for selecting products suitable for different purposes. It is of particular value for bitumens used in thick films, for example, in cable-joint and battery boxes, as crack fillers, and as protective coatings for roofs, ships, electric cables, steel water mains, refrigeration chambers, etc. When the bitumen is to be used in very thin films, however, such as in paving mixtures, the softening point has little significance by itself, but in conjunction with other properties, such as penetration, is most useful for indicating susceptibility characteristics.

The Relation between the R and B Softening Point and Viscosity

The smooth shape of bitumen viscosity–temperature curves in general indicates that the softening point does not represent a temperature at which viscosity changes with any rapidity.

Particular interest in the relation between the softening point and viscosity has been evinced by several investigators. Thus, the Academy of Science at Amsterdam in 1935 regarded the R and B softening point as being merely that temperature at which any asphalt attains a definite viscosity of approximately 12,000 poises, despite a report by Saal [80] that viscosity values between 8000 and 20,000 poises had been recorded. Traxler and his co-workers [96] later reported values ranging from 14,000 to 30,000 poises.

On the other hand, for pitches, Fuidge and Deadman [28] considered the softening point as representing a definite equiviscous temperature, at which the steel ball falls through the softened pitch in a few seconds and is equivalent to about 1400 seconds on the standard tar viscometer (*i.e.*, about 5600 poises). Here again, however, this is refuted by computations made by the present author from results recorded by Fair and Volkmann,[24] values varying from about 14,000 to 39,000 poises being obtained. These values have been calculated from the position of the softening point on a series of viscosity–temperature curves. Further experimental evidence and theoretical discussions on this issue are presented in the later parts of this work.

It is significant that Klinkmann [40] found that the softening point was dependent not only on the viscosity of the material under test, but was directly proportional to its surface tension and rate of temperature change and inversely proportional to the specific gravity.

Saal and Koens [83] also pointed out that the R and B determination is carried out at a steadily increasing temperature, so that the temperature in the bitumen may be somewhat lower than that of the surrounding water. It is probable therefore that with entirely different temperature coefficients there may be differences in the viscosity at the softening point. Moreover, the thermal conductivities of different bitumens may vary widely and decrease with rise in temperature,[82] and probably therefore also influence

the actual temperature at which the ball begins to fall through the bitumen. In effect, the softening point may be regarded as a resultant measure of consistency, heat capacity, thermal conductivity, and density, all of which vary with temperature.

Traxler, Schweyer, and Romberg,[105, 106] in studies of the rheological significance of the test, have indicated from a consideration of the physics involved that the viscosity at the softening point cannot be constant. In the first place the R and B method is shown to combine the principles of a falling-ball viscometer and those of a falling-co-axial-cylinder viscometer, the mass of bitumen being moved in a shearing action similar to that in the latter type. Then again, the variation in the rate of shear during the test must also affect the numerical value of the viscosity for non-Newtonian liquids, as has been pointed out in an earlier part of the present discussion.

The same investigators have also attempted to show that one straight line is obtained when log viscosity (in poises) at 77° F is plotted against the R and B softening point for a number of steam-refined and air-blown asphalts. The relationship has been expressed mathematically as :—

$$\log \eta_i = 0{\cdot}0543\, M - 0{\cdot}232 \quad . \quad . \quad . \quad . \quad \text{(VII)}$$

where M is the R and B value in ° F;
η_i is the viscosity in poises.

Their calculated values agree to within ±17 per cent of the experimentally determined results for the samples considered. The relatively large deviations are, however, not regarded as unreasonable by Traxler and his associates, and are attributed in the first place to the lack of sensitivity of the R and B method of test—a difference of 1° F in softening point can account for a difference of about 1 per cent in the viscosity based on equation (VII)—and to a smaller degree to experimental errors in the viscosity measurements.

It is significant that these workers appear to be satisfied with their own relationship over the range 10^4 to 10^9 poises. They do not, however, go so far as to recommend this as an empirical conversion of R and B softening point to absolute viscosity, because of the unknown limitations of the equation which they themselves state does not hold for vacuum or steam-refined asphalts of very high temperature susceptibility.

The present author disagrees with the finding that only one equation is applicable to all bitumens. Traxler and his co-workers obviously based their conclusions on scanty information obtained with too few representative samples.

Part II of the present work, carried out on numerous samples, shows clearly that there is a specific straight line for each *class* of bitumen manufactured from a given parent oil in which a regular series of samples has been drawn off as the bitumen becomes steadily harder and harder with increased processing. The positions of the lines in relation to the two axes are dependent upon the nature of the materials, and may be far apart for widely different classes.

It is unfortunate that Traxler and his associates worked with samples which occupied positions so close as to suggest a common relationship for all types of bitumens.

The present author has found that an improved direct relationship is obtained if the logarithm of the softening point is used as one of the axes rather than plain softening point itself as suggested by Traxler *et al.* A different equation, however, applies to each type of material according to its characterization index based on the relation between its penetration and softening point.

The general equation for each characteristic line can be expressed thus :

$$\log \eta = a - b \log M. \quad . \quad . \quad . \quad . \quad . \quad \text{(N VII)}$$

where a and b are characteristic constants for each class of material.

Values for a and b have been ascertained by the author for different classes of bitumen, and are reported in Part II.

The Penetration Test

ASTM D5; *IP* 49.

The term " penetration " as applied to a bituminous material is a measure of its consistency, and is expressed as the distance (in tenths of a millimetre) that a needle of standard dimensions penetrates vertically into a sample of the material under fixed conditions of loading, time, and temperature.

Where the conditions of testing are not specifically stated, the load, time, and temperature are understood to be 100 g, 5 sec, and 77° F respectively, but under special circumstances other conditions may be employed to increase the sensitivity. This is often advisable for very hard bitumens, where the penetration is so small that the magnitude of error involved in the normal experimental procedure becomes appreciable and a larger reading desirable. For example, a combination of 200 g, 60 sec, at 32° F is useful for measuring the consistency of particularly hard samples at a low temperature, whilst 50 g, 5 sec, at 115° F is sufficiently sensitive for soft materials measured at a fairly high temperature.

The requirement of reproducibility laid down by the Institute of Petroleum is not more than 2 units mean difference for penetrations less than 80, not more than 2·5 per cent of the mean for penetrations between 80 and 225, and not more than 3·5 per cent above 225 pen.*

There are a number of factors affecting the measurement of penetration. For example, hysteresis effects associated with this test have been examined by Woog and others.[113] Prolonged periods of cooling at atmospheric temperature (*e.g.*, 14 hr instead of the standard of 1 hr) result in figures 15 per cent too low. Free circulation of the air during cooling and thorough agitation of the water-bath are particularly stressed.

Besides the load, time, and temperature, other factors include the surface-tension and viscosity characteristics of the bitumen and also the dimensions of the needle. Disparities in the determinations may also be due to inadequate adhesion between the needle and bitumen as a result of a protective film of water surrounding the needle. This effect, though not

* *Pen* is the recognized abbreviation of *penetration*. The terms *ASTM Penetration*, *IP Penetration*, or *Standard Penetration* are regarded as synonymous in this work, but as a matter of habit and convenience, a preferential use is shown for the expression *ASTM Penetration*.

very great, tends to give high results. Under conditions of brittleness in the bitumen, there is also a possibility of the needle breaking its way rather than penetrating smoothly through the bitumen.

It is worth noting that for penetrations below 20, any experimental error due to failure to adjust the point of the needle at the exact surface of the bitumen may be large in proportion to the numerical value of the penetration figure. For penetrations above about 150, there is an increasing frictional resistance to the needle's descent, which probably introduces a steadily increasing error in the theoretically correct penetration reading.

Saal and Labout [84] have demonstrated the effect of the elastic behaviour of bitumens on the penetration value by periodic interruptions of a series of tests, in which the penetration depths are increased as a consequence of the dissipation of the elastic tension during interruption. The differences between the normal and interrupted test values are an indication of the degree of elasticity, non-elastic bitumens giving identical results, slightly elastic materials small differences, whilst highly elastic bitumens are clearly marked. Thixotropy in bitumens also has a definite effect on penetration results.

The necessity for rigid adherence to the standard procedure specified for the test becomes evident from the above considerations.

Knowles and McCoy,[41] in a study of the surface characteristics of asphalts, have modified the penetration-test method to suit their specific purpose by determining the weight required to force the ASTM penetrometer needle into a layer of asphalt to a given depth in a constant time (also 5 sec).

Relationship between Penetration and Temperature

The following four empirical factors based on differences in penetration obtained by varying the conditions of load, time, and temperature have been proposed to indicate the susceptibility of asphalts to temperature change. The first two have received official recognition from the ASTM (D5), whilst the third has been suggested by Holmes, Collins, and Child.[36] The fourth has been included in the specification of one of the States of the U.S.A.[51] :—

$$(a)\quad \text{S.F.} = \frac{\text{Pen at } 115^\circ \text{ F (50 g, 5 sec)} - \text{Pen at } 32^\circ \text{ F (200 g, 60 sec)}}{\text{Pen at } 77^\circ \text{ F (100 g, 5 sec)}} \quad \text{(Factor E)}$$

$$(b)\quad \text{S.F.} = \frac{\text{Pen at } 100^\circ \text{ F (100 g, 5 sec)}}{\text{Pen at } 77^\circ \text{ F (100 g, 5 sec)}} \quad \text{(Factor F)}$$

$$(c)\quad \text{S.F.} = \frac{\text{Pen at } 77^\circ \text{ F (100 g, 5 sec)}}{\text{Pen at } 32^\circ \text{ F (200 g, 60 sec)}} \quad \text{(Factor G)}$$

$$(d)\quad \text{S.F.} = \frac{\text{Pen at } 39{\cdot}2^\circ \text{ F (200 g, 60 sec)}}{\text{Pen at } 77^\circ \text{ F (100 g, 5 sec)}} \quad \text{(Factor H)}$$

These susceptibility factors have been criticized by Traxler and his associates [85, 103] on the grounds that they measure susceptibilities under unknown and varying stresses which change at different rates. Different loadings and lengths of time for factors E, G, and H complicate the issue even more. In addition, the factors can hardly be expected to compare

the susceptibilities of bitumens of differing consistencies, because they do not measure rate of change of consistency with temperature. Again, the factors can only be applied to materials which do not have penetrations higher than 350 at 100° or 115° F under the test conditions. Thus, materials softer than about 75 pen under normal conditions at 77° F cannot be examined at the higher temperatures. It has also been shown [36] that whilst factors E and F often give results of the same order of magnitude, they are just as often not in agreement.

According to its originators, factor G has distinct advantages over the others in that, it is not limited to fairly hard bitumens and can be used for the whole range of penetrations. It is aimed specifically at supplying information on changing characteristics at subnormal temperatures.

It is of interest to note from the work of Bencowitz and Boe [6] that the ratios of penetrations found with different weights are practically constant. Thus, over the temperature range 32° to 104° F, the mean ratios for penetrations carried out with 100-g as compared with the 50-g, 200-g, and 250-g are respectively 1·74, 0·677, and 0·568.

It is thus possible, for example, to use 200 g for hard bitumens and 50 g for soft bitumens and to convert the results to the 100-g basis by means of the appropriate factor. Direct comparisons of susceptibility can also be made at different temperatures with 50 g for soft materials, 100 g for intermediate, and 200 g weight for hard.

From this it would appear that susceptibility factors E, F, G, and H are not based on irrational bases, as has been considered by a number of workers. These methods have not proved of much value,[51] however, and others have been suggested based on more fundamental data obtained from carrying out penetrations at a number of temperatures.

In this connexion, Bencowitz and Boe [6] have shown that the penetration of a bitumen at different temperatures can be expressed by the following form of equation :—

$$P = A + B.C^t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(VIII)}$$

where P is the penetration at temperature $t°$ C;
A, B, and C are constants.

The equation can be solved for constants, A, B, and C for any particular asphalt by obtaining at least three different penetrations, preferably over a wide temperature range.

It follows that :—

$$\log (P - A) = t \log C + \log B = mt + k \quad . \quad \text{(VIIIA)}$$

where m and k are new constants.

Therefore, if log $(P - A)$ is plotted against temperature, a straight-line relationship should be obtained.

The value of A is shown to be relatively small compared with P. Therefore, it is justifiable to plot log penetration directly against temperature particularly over wide ranges, so that :—

$$\log P = mt + k \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(IX)}$$

According to Bencowitz and Boe, the true susceptibility is represented by the differential dP/dt, but, since " it is customary to express the sus-

ceptibility as some sort of ratio, which involves the actual penetration in addition to the change in penetration," these authors have decided to define susceptibility by the coefficient $1/P \times dP/dt$.

If this is expressed as a definite integral between the limits of temperature t_2 and t_1, their proposed index becomes $P_2 - P_1/P_t$, where P_t is the penetration at the average temperature of the range. The authors then show that this ratio is valid only when similar types of asphalt are compared, but discordant results are obtained for large groups of asphalts. The reason for this is stated to be due to the " coefficient being unfortunately not a constant owing to the differential dP/dt." They then propose that the index $(P_2 - P_1)$ alone be taken as an approximation.

i.e., Susceptibility Index of Bencowitz and Boe

$$= \int_{t_1}^{t_2} \frac{dP}{dt} \cdot dt = P_2 - P_1 \quad . \quad . \quad . \quad \text{(Factor J)}$$

Thus, according to this system, only two penetrations are required at specified temperatures; but it must be borne in mind when comparisons are made between different asphalts that the temperature ranges in all instances must be the same. Bencowitz and Boe have compared the indices for a number of materials over the ranges 0° to 25° C, 0° to 40° C, and 0° to 50° C respectively, and have not only found differences in the order of the results in the three cases, but have also noted that some asphalts are more susceptible than others over one part of the temperature range and less susceptible over another.

In the present author's opinion, the reasoning of Bencowitz and Boe has been founded on an illogical basis, since the index should obviously have a logarithmic form for the penetration to conform to the original equation (IX). The corrected susceptibility differential should thus be :—

$$d \log P/dt$$

and the revised index of Bencowitz and Boe should then be

$$\text{S.I.} = \log P_2 - \log P_1 \quad . \quad . \quad . \quad \text{(Factor NJ)}$$

The incorporation of the correction factor A in equation (VIII) has also not been found necessary by other workers, and it is now generally accepted [11 (discussion), 33, 51, 69] that the changes in consistency between 32° F and the R and B temperature can be expressed reasonably by equation (IX), particularly if the allowable test limits of the penetration test itself are taken into account.

Lewis and Welborn [51] consider that the slope of the log penetration–temperature curve is a true index of susceptibility.

Thus,
$$\text{S.I.} = m = \frac{\log P_2 - \log P_1}{t_2 - t_1} \quad . \quad . \quad . \quad \text{(Factor K)}$$

Elaborating upon this index, these investigators show that the slope can readily be calculated from the curve by finding the temperatures of the asphalt at penetrations of 10 and 100, so that :—

$$\text{Slope} = \frac{\log 100 - \log 10}{t_2 - t_1} = \frac{2 - 1}{t_2 - t_1} = \frac{1}{t_2 - t_1} = S.I. \quad . \quad \text{(Factor L)}$$

where t_2 and t_1 are the temperatures in ° F corresponding to penetrations of 100 and 10 respectively.

The present author prefers to modify this expression in his own work and uses its reciprocal, so that the " Penetration Susceptibility Factor " used later in this work can be defined directly as the temperature differential over which the penetration changes from 100 to 10.

Thus $$\text{P.S.F.} = t_{\text{pen}}\,100 - t_{\text{pen}}\,10 \quad . \quad . \quad \text{(Factor NL)}$$

It should be noted that in actual fact there is no essential difference between relationships (NJ) and (NL) respectively, since both are based on the slope m in factor (K), but in the former case the temperature differential is made into a constant, while in the latter ($\log P_2 - \log P_1$) becomes a constant.

Grant and Hoiberg,[29] in discussing the work of Lewis and Welborn, consider that their index is in fact not a true measure of bitumen susceptibility, since different depths of penetration correspond to different shearing stresses. They add, however, that this method may actually be more closely related to service behaviour than a true susceptibility measured at a constant shearing stress, for the stresses obtained at different temperatures with the penetrometer may conceivably be proportional to those acting in service at the corresponding temperatures.

The Penetrometer Method for the Measurement of Flow Properties

From theoretical considerations,[80] and on the basis of tests conducted on two steam-distilled bitumens, Saal and Koens [83] concluded that the empirical relationship between penetration measurements and absolute viscosity for " non-plastic asphaltic bitumens " can be expressed by :—

$$\eta = 5{\cdot}13 \times 10^9/\text{Pen}^{1{\cdot}93} \text{ poises} \quad . \quad . \quad . \quad . \quad . \quad \text{(X)}$$

Thelen [94] showed that the flow properties of bitumens can be satisfactorily evaluated by means of the penetrometer if a succession of penetration readings is made without touching the needle or sample between each reading.

The lower extremity of the penetrometer needle is not perfectly conical in shape, but is in fact a truncated cone. For this reason there is a tendency for erratic results to be obtained with bitumens of low penetration value, arising from the natural greater resistance to penetration offered by a hard bitumen to a flat-surfaced object of relatively large cross-sectional area as compared with a perfect conical needle of negligible area at the instant when penetration commences but progressively increasing in area with depth.

Thelen accordingly based his equations on penetrations greater than 43, at which point he considered the cylindrical portion of the needle to be partially immersed in the bitumen.

Rhodes and Volkmann,[77] however, pointed out certain fallacies in Thelen's deductions, and also proved that the true frustrum height of the penetrometer needle tip is 54, and not 43. They then analysed Thelen's experimental results, and demonstrated that the test conditions were comparable with those prevailing in the falling-coaxial-cylinder viscometer.

The penetrometer method was accordingly shown to be satisfactory for the determination of absolute viscosity. From a consideration of the theory based on axial displacement of concentric vertical cylinders, the following relationship was derived :—

$$\eta = (1{\cdot}25 \times 10^9) \times (t_f - t_i)/(P_f + P_i - 46)\,(P_f - P_i). \quad \text{(XI)}$$

where P_f and P_i are the final and initial penetrations respectively;
$(t_f - t_i)$ is the time interval in seconds.

By consideration of the normal standard ASTM penetration test as a special case where $P_i = 0$; $t_i = 0$; and $t_f = 5$, these investigators showed that their relationship could be reduced to an equation remarkably similar in character to Saal's empirical formula. Thus

$$\eta = 6{\cdot}25 \times 10^9/P(P - 46) = 6{\cdot}25 \times 10^9/\text{Pen}^2 - 46 \times \text{Pen} \quad . \quad \text{(XII)}$$

Since this relationship was derived for the cylindrical shank of the needle and not for the conical portion, Rhodes and Volkmann themselves acknowledged limitations therein.

Traxler and his co-workers [100, 101] inquired into the validity of these formulæ by carefully conducted studies of the rheological properties of certain bitumens specially selected as most closely approaching materials of viscous flow characteristics. They found that, in general, a fairly straight line was obtained if log viscosity was plotted against log penetration, though a sinuous form of curve was probably more correct over wide ranges. Each bitumen, however, gave a separate line differing from that of the other samples and consequently also from the line representing the Saal formula. That is, different bitumens of the same penetration do not all have the same viscosity, as might be inferred from the empirical relationship. Moreover, Saal's equation was based on variations in penetration-viscosity data obtained on only two related samples simply by changing the temperature of the determinations. Traxler and his associates showed that different results are obtained for a series of bitumens in which the consistency is varied by altering the extent and degree of processing. They concluded, therefore, that the equation of Saal and Koens gives only rough approximations of viscosity.

In later work, Traxler *et al*,[99, 105, 106] gave various reasons to show that the method of successive penetrations is also rheologically unsound, though it has some value from a practical point of view because complex-flow bitumens can be examined over a range of shear rates not easily available in absolute viscometers. For example, it can be extremely useful in age-hardening studies, since a number of tests may be performed on a single sample of hard bitumen without appreciably disturbing it.

Mack,[55] however, points out that the criticism of Traxler and his associates is not justified because their viscosity measurements were carried out at shearing stresses which were considerably lower than those prevailing during the penetration determination, and the viscosity of plastic asphalts is known to vary with the shearing stress. In fact, the percentage difference between the observed and "apparent" viscosity calculated according to Saal's formula (or otherwise) is regarded by Pfeiffer and van Doormal [69]

and by Broome [12] as a measure of the plasticity of a bitumen under the conditions of the determination. Thus :

$$\text{Degree of Plasticity} = 100(V_{obs} - V_{calc})/V_{obs} \quad . \quad \text{(XIII)}$$

The work of Saal and Koens [83] and of Pfeiffer and van Doormaal [69] has shown that there is a linear relationship between the logarithm of the penetration depth and the logarithm of the penetration time. These lines differ in slope, which is steepest in the case of those bitumens exhibiting almost purely viscous flow and flattest for the most plastic. The general relationship is thus

$$\log \text{pen} = c \log \text{time} + \text{constant} . \quad . \quad . \quad . \quad \text{(XIV)}$$

This equation can also be expressed mathematically in an exponential form, which Mack [55] has applied to the method of successive penetrations, so that

$$P = P_1 t^c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XIVA)}$$

where P is the total penetration at total time t;
P_1 is a constant representing the penetration at time $t = 1$ second;
c is another constant relating to the flow properties of the bitumen under test.

Mack [56] has also shown that plastic flow can in general be represented by the equation

$$\eta = F^n/R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XV)}$$

where η is the viscosity of the plastic system;
F is the shearing stress in dynes per sq. cm.;
R is the rate of shear in reciprocal seconds;
n is a constant identifying the type and degree of plastic flow.

The constant c in equation (XIV) is a function of n in equation (XV), which defines the rheological properties as follows :—

$$n = (1/c) - 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XVI)}$$

(*a*) If $c = 0{\cdot}5$, then $n = 1$, which is the condition of purely viscous flow;
(*b*) If c is less than 0·5, n is greater than 1, and the flow is plastic;
(*c*) If c is greater than 0·5, n is less than 1, which is indicative of dilatancy.

Thixotropy can also be detected in a quantitative way in bitumens after ageing by an increase in the value of c over that of the unaged materials. Since the time interval between successive penetrations allows for partial recovery of the elastic deformation, the elastic properties can be measured by taking a series of individual penetrations for various lengths of time. In the case of viscous bitumens, practically the same penetration is obtained for a given time by the individual as well as the cumulative method of testing, while plastic materials, with elastic properties, have lower penetrations by the individual than by the cumulative method. Differences in the value of c ascertained by both methods thus serve as an estimation of the degree of elasticity.

Mack has also shown by a mathematical derivation that equation (XIV) can be used as a basis for relating viscosity and penetration, thus :

$$\eta = A.L.t/CP^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XVII)}$$

where A and C are constants, L = constant load, and t = time in seconds.

Relative viscosity can therefore also be expressed by the time in seconds required for a given penetration. It follows from equation (XVII) that where the load and time remain constant as in the standard penetration test where $L = 100$ g and $t = 5$ sec, bitumens of different flow properties have the same viscosity when :—

$$CP^2 = C_1P_1^2 = C_2P_2^2 \quad . \quad . \quad . \quad . \quad \text{(XVIII)}$$

The Work of Pendleton

Probably the most valuable contribution to the use of the penetrometer method for measuring the flow properties of high-viscosity fluids has been made by Pendleton.[67] This worker points out that each absolute viscosity determination by the moving-cylinder method requires an average time of one day, while a complete set of readings can be made in about 15 min by means of the penetrometer. In addition to speed of operation and precision, the method has the great advantage of reproducibility without extensive heat treatment and pre-working. This point is most important, since the amount of working is probably the chief disturbing factor in determining the flow properties of materials of high consistency.

Use of a succession of time intervals in the penetrometer test with one load can furnish sufficient data for obtaining a complete set of curves relating rate of shear with shearing stress.

The theory has been developed to a point where absolute viscosities may be determined both for viscous flow (viscosity independent of rate of shear) and for " generally viscous flow " (in which viscosity is dependent upon the rate of shear).

Pendleton has shown that the earlier formulæ, based on viscous flow, are not valid when applied to fluids in the viscosity range 10^6 to 10^{12} poises, where the flow is " generally viscous." The penetrometer has been found to work admirably in this range, provided extensions are made to time and load, which are limited in the standard ASTM Method.

The theory is dependent upon certain assumptions :—

(*a*) It is considered that the amount of asphalt displaced by the penetrating needle is negligible.

(*b*) Elastic effects in the penetrometer method are also considered to be negligible when compared with those in most absolute viscometers.

(*c*) The relationships are derived in terms of the area of an assumed hypothetical hollow cylinder of the same diameter as the penetrometer needle with an infinitely thin wall and frictionless interior. To adapt the equations to the standard needle, a correction factor is subtracted from the depth of penetration based on the premise that the lateral area of the cylinder is equivalent to the area of the needle in contact with the asphalt.

The standard dimensions of the penetrometer needle have been used by Pendleton to calculate the length of the equivalent cylinder. This has

been computed as approximately 31 dmm as against 54 dmm for the overall length of the truncated cone portion. A negative correction of 23 must therefore be made for all penetrations above 54.

Obviously for penetrations below 54, the correction must be a variable depending upon the depth of the penetration. An analysis, by Pendleton, of the surface relationships calculated from the standard dimensions of the penetrometer needle gives the following general correction for the needle point in dmm

$$K' = P(0{\cdot}849 - 0{\cdot}00788\,P) - 0{\cdot}0562 \quad . \quad . \quad \text{(XIX)}$$

Pendleton has correlated the penetrometer method with the capillary viscometer for viscous flow and has demonstrated that penetration values can be converted to poises by a general relationship similar in form to Mack's equation (XVI).

Thus, $\quad$ Viscosity $\eta = [Mt/P(P - K')]\,1{\cdot}25 \times 10^7$ poises $\quad . \quad$ (XX)

where M is the load used in the penetration test;

t is the time;

P is the penetration in dmm;

K' is the correction to the penetration value to allow for the shape of the needle point.

Under the normal conditions of the penetration test, $M = 100$ g and $t = 5$ sec, so that equation (XX) becomes

$$\eta = 100 \times 5 \times 1{\cdot}25 \times 10^7/P(P - K') = 6{\cdot}25 \times 10^9/P(P - K') \quad . \quad \text{(XXI)}$$

It is noteworthy that this equation is identical in every respect to equation (XII) derived by Rhodes and Volkmann [77] except for the value of the constant K'.

The present investigator has taken over at this point in the Pendleton theory and has calculated :—

(i) the viscosities in poises equivalent to the full range of ASTM penetrations;

(ii) the actual corrections to be subtracted from all ASTM penetrations up to 54.

Pendleton's equation (XIX) has been used for the correction factor K', from which equation (XXII) has been derived as follows :—

$$\eta = 6{\cdot}25 \times 10^9/0{\cdot}00788\,P^3 + 0{\cdot}151P^2 + 0{\cdot}0562P \text{ poises} \quad . \quad \text{(XXII)}$$

This equation has been evaluated for various values of P from which the accompanying Table II has been drawn up. For convenience of plotting and reference purposes, a column has been included to show log viscosity in poises. This table is of fundamental importance in the present work, and has been used in the experimental investigations reported in Part II onwards.

The graphical relationship between log viscosity in poises and log ASTM penetration, based on the analysis of Pendleton is depicted in Fig 1. It is interesting to note there is a distinct point of inflexion at 54 pen, where the curve changes its shape from being slightly concave (in the section from

1000 pen down to 54 pen) to convex (in that portion from 54 pen down to below 1 pen).

This curve will be referred to again during the discussion on the experimental work (see Part IV).

TABLE II

Conversion of ASTM Penetration Values into Poises

(Values derived by the author from Pendleton's Analysis)

Penetration	Viscosity in poises	Log viscosity in poises
1000	$6{\cdot}40 \times 10^3$	3·8062
800	$1{\cdot}01 \times 10^4$	4·0043
600	$1{\cdot}80 \times 10^4$	4·2553
400	$4{\cdot}15 \times 10^4$	4·6180
300	$7{\cdot}51 \times 10^4$	4·8756
200	$1{\cdot}76 \times 10^5$	5·2455
150	$3{\cdot}38 \times 10^5$	5·5289
100	$8{\cdot}13 \times 10^5$	5·9101
80	$1{\cdot}37 \times 10^6$	6·1367
60	$2{\cdot}82 \times 10^6$	6·4502
40	$8{\cdot}36 \times 10^6$	6·9222
30	$1{\cdot}784 \times 10^7$	7·2514
20	$5{\cdot}017 \times 10^7$	7·7004
10	$2{\cdot}658 \times 10^8$	8·4245
8	$4{\cdot}420 \times 10^8$	8·6454
6	$8{\cdot}37 \times 10^8$	8·9227
4	$1{\cdot}988 \times 10^9$	9·2985
3	$3{\cdot}59 \times 10^9$	9·5551
2	$8{\cdot}02 \times 10^9$	9·9042
1	$2{\cdot}905 \times 10^{10}$	10·4631

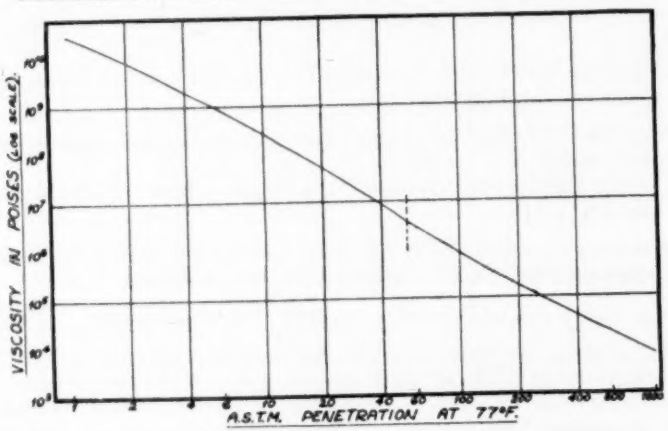

FIG 1

PENETRATION–VISCOSITY RELATIONSHIP CALCULATED FROM PENDLETON'S EQUATION

In order to prove the accuracy of his deductions, Pendleton made a critical survey of the formulæ of Saal and Koens [equation (X)], of Rhodes and Volkmann [equations (XI) and (XII)] and of Mack [equation (XVIII)] on the basis of certain experimental data for a coal-tar pitch presented by

Rhodes and Volkmann.[77] Curves were plotted relating the viscosities in poises calculated by each method from a series of successive penetrations for time intervals of 5 sec. The values in each case were compared with the absolute viscosity determined by means of a capillary viscometer. The results demonstrated conclusively that the Rhodes and Volkmann formula provides for too high a correction for the shape of the needle point, while the curves for the uncorrected equation of Saal and Mack respectively show a slope in the reverse direction. On the other hand, the points calculated by Pendleton's equation (XX) are all within 2 per cent of the observed value.

In order to ascertain the reliability of Table II for the direct conversion

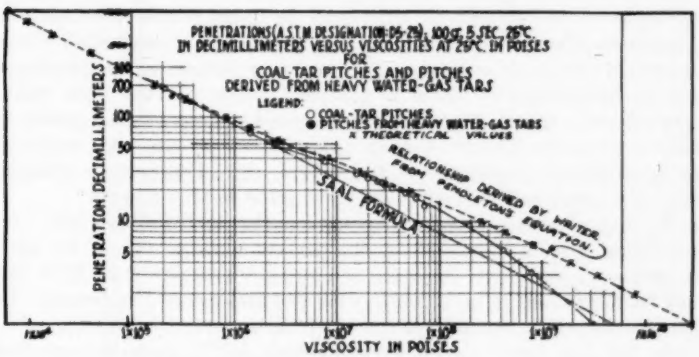

FIG 2

COMPARATIVE DETERMINED AND CALCULATED PENETRATION–VISCOSITY RELATIONSHIPS

of ASTM penetration values into poises, the present author, in his turn, has made use of other experimental data given by Fair and Volkmann.[25] Fig 2 is a modification of the original diagram appearing in the published work of Fair and Volkmann, and shows the actual viscosities determined by them with a falling-coaxial-cylinder instrument for two series of coal-tar and water-gas-tar pitches as compared with the equivalent viscosities calculated from the Saal formula. The present investigator has superimposed on the same chart the theoretical values shown by him in Table II.

An inspection of these curves shows clearly that the theoretical viscosities calculated from the Saal formula and from the writer's consideration of Pendleton's analysis agree reasonably well with the observed experimental data for all penetration values above 54. Below this point, however, there is an appreciable divergence between the observed viscosities and the values derived theoretically from the Saal equation. The reasons for the deviations have already been discussed.

The equivalent Pendleton viscosities, on the other hand, appear to be slightly on the high side throughout, but the curves are remarkably similar in shape down to below 20 penetration. The degree of divergence over that range is on the whole within the limits of experimental error of the penetration and viscosity determinations. In fact, the agreement can be regarded as reasonable right down to 10 penetration, particularly if due

allowance is made for the practical difficulties peculiar to penetration testing of such hard materials. The large divergence below 10 penetration is understandable, and is in accord with the writer's observations that the practical useful limit of the penetrometer is reached at approximately 10 penetration.

True Penetrations : A New Conception by the Author

It follows from the foregoing discussion that the standard ASTM penetration units are unscientific in basis, since empirical factors are involved which depend on certain needle dimensions fortuitously laid down in the test method and accepted universally as a standard in asphalt technology. Penetration values should be expressed in units which are independent of extraneous effects. This does not imply that the present author regards the standard truncated-cone shape of the lower portion of the penetrometer needle as unsatisfactory from a practical point of view, but that the *penetration units should*, if possible, *be converted to a more logical system which postulates a regular cylindrical-shaped thin-walled penetrometer needle which offers no frictional resistance or end effects, etc.* Pendleton's analysis as already discussed has proved to be invaluable in this respect.

In the first place it is necessary to convert the ASTM values into " true " penetrations, a term suggested by the present author. Thus, for all standard penetrations above 54 dmm a constant correction of 22·8 dmm * should be subtracted in accordance with the findings of Pendleton. Below 54 penetration the correction factor is given by equation (XIX).

Table III has been compiled to convert ASTM penetrations directly into true values.

Table III

Conversion of ASTM Penetration Values into True Penetrations

(As Proposed by the Author)

ASTM penetration	Correction factor	True penetration
300	22·8	277·2
54	22·8	31·2
50	22·7	27·3
45	22·2	22·8
40	21·3	18·7
35	20·0	15·0
30	18·3	11·7
25	16·2	8·8
20	13·9	6·1
15	10·9	4·1
10	7·7	2·3
5	4·0	1·0
1	0·8	0·2

* The corrections have all been calculated to include the first place of decimals, though the degree of precision of the penetration test does not warrant such accuracy. This has, however, been done in the present instance to avoid unnecessary mathematical errors, particularly for the lower penetrations, where the value 22·8 is more accurate than the whole number 23 mentioned previously.

The relationship is shown graphically in Fig 3 from which the following points arise :—

1. The portion *PQ* from 10 pen (ASTM) to 54 pen is almost perfectly linear.

2. The portion *QR* is slightly curved from 54 pen to about 300 pen, above which the curve becomes asymptotic to the line of equality between ASTM and true penetrations.

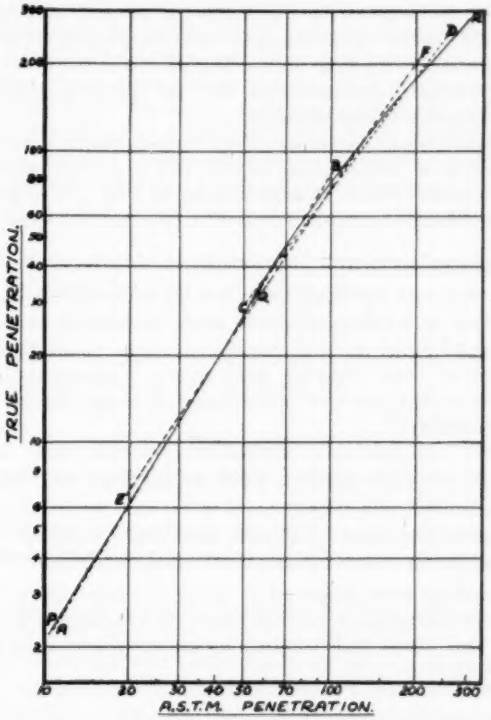

FIG 3

RELATIONSHIP BETWEEN ASTM AND TRUE PENETRATIONS

3. The dotted line *AB* shows that that portion of curve *PQR* between the ASTM penetration values of 10 and 100 respectively is reasonably straight within the limits of possible experimental error.

4. Similarly a linear relationship (dotted line *CD*) is experimentally applicable to ASTM penetration limits of approximately 54 and 250 respectively.

5. For many practical purposes, a straight-line relationship can even be used as a fair approximation for the whole range of penetration bitumens (between 20 and 200 pen) without introducing errors considerably greater than those allowed by the test procedure. This is evident from line *EF*, which shows that the error is on the positive

side below 54 pen, negative from about 54 to 150 pen, and positive again above that value.

The foregoing considerations indicate that it is definitely more logical mathematically to use the logarithms of true penetrations rather than of ASTM values in the plotting of penetration data against other properties. It is, however, often more convenient in practice to use ASTM values, the penetration range under consideration then determining the degree of reliability as under points 1 to 5 above. Since proportionality exists under various limits between the logarithms of the true and ASTM penetrations respectively, either of these can be used for presenting graphical data. The choice depends at any time on the degree of accuracy pertaining to the relevant experimental determinations and on the significance and use of the particular graphical relationships.

Where wide penetration ranges are under consideration, it can be anticipated that the logarithm of ASTM penetrations will in general give two distinct portions of the total curve, intersecting at 54 pen. This point will be in evidence in the discussions on the present experimental work (see Part II).

Relationships between Penetration and Softening Point

The penetration test by itself does not disclose effects of deformation, but in conjunction with other empirical tests, such as the R and B softening point, it can be of great use for the classification of bitumens as to their relative deviation from viscous behaviour. Characterizations of this nature have the added practical advantage of being simple, rapid, and of universal applicability.

There are two well-known classification methods which fall under this heading and which have gained wide recognition as standards in the evaluation of bitumen quality :—

(*a*) penetration index of Pfeiffer and van Doormaal; [69]
(*b*) penetration index of Holmes, Collins, and Child.[36]

Both relationships were proposed at about the same time, but the derivations are entirely independent of each other, and in view of their importance in Part III of this work, their evolutions are fully discussed below.

Pfeiffer and van Doormaal Penetration Index (P.v.D. Index)

Pfeiffer and van Doormaal [69, 70] have proposed a scheme for the classification of bitumens according to a penetration index founded in the first place on the validity of the following two relations which have already been discussed.

(i) Saal's equation for the conversion of penetration into viscosity.

$$\eta = 5{\cdot}13 \times 10^9/\mathrm{Pen}^{1{\cdot}93} \text{ poises} \quad . \quad . \quad . \quad . \quad \text{(X)}$$

(ii) The viscosity at the R and B softening point is approximately 12,000 poises.

If these two formulæ are equated, it can be shown that the penetration at the R and B softening point should be approximately 800.

If this assumption is correct, it follows that the slope of the log penetration–temperature curve is

$$\alpha = \log 800 - \log \text{pen at } 77^\circ \text{ F/R and B Soft. Pt.} - 77^\circ \text{ F} \quad . \quad \text{(XXIII)}$$

Pfeiffer and van Doormaal have constructed a nomogram (Fig 4) * in which the numerator and denominator of equation (XXIII) are plotted in opposite directions on two parallel scales at a given distance from each other. They have shown that the position of any point on the straight line joining the 77° F point on the denominator scale with the 800 penetration point on the numerator scale fully characterizes all bitumens of different hardness but having the same slope according to the equation. In other words, there is a characteristic point for all bitumens which have the same susceptibility to change in penetration with change in temperature.

The proportions of the scale of the softening-point temperatures and penetration values in Pfeiffer and van Doormaal's chart have been selected so that a change in log penetration of one unit is exactly equal in length to a change of 90° F (50° C) on the softening point scale. The line joining the 77° F with the 800 pen points has then been divided into thirty equal parts to indicate various degrees of susceptibility. The fifth point starting from the temperature scale has arbitrarily been assigned the "penetration index" of —5, . . . the tenth the index 0, . . . and the twentieth the index + 10.

From this it follows geometrically that the slope α, for the above chosen scales, can be expressed by the following relation :

$$\alpha = \tfrac{1}{90}\,(20 - \text{P.I.})/(10 + \text{P.I.}) \quad . \quad . \quad . \quad \text{(XXIV)}$$

Equation (XXIV) can then be written in another way to give the penetration index directly, in terms of the slope α :—

Thus :

$$\text{P.I.} = (30/1 + 90\alpha) - 10 \quad . \quad . \quad . \quad \text{(Factor M)}$$

The value of α can be obtained from equation (XXIII).

Since there are only two variables in the combination of equations (XXIII) and (M) respectively, it is evident that the P.v.D. penetration index is a direct function relating only penetration at 77° F with the R and B softening point.

In practice, it is rather inconvenient to use the nomogram, and it is preferable to read off penetration indices directly from a simple chart drawn up by Pfeiffer and van Doormaal from their nomogram (see Fig 4, Chart B).

These investigators have used the differences in temperatures susceptibility of asphaltic bitumens to classify them into three main groups merging into one another, the boundaries of which have been chosen more or less arbitrarily.

Class 1.—N Type : Index between —1 and 1.
Normal straight-run bitumens, steam or vacuum refined.

Class 2.—Z Type : Index below —1.
Coal-tar pitch type; characterized by great susceptibility and great brittleness.

Class 3.—R Type : Index above +1.
Blown bitumen type; characterized by low susceptibility and slight brittleness.

* In view of the importance of the P.v.D. Index in the present work, the original chart has been reproduced for reference purposes.

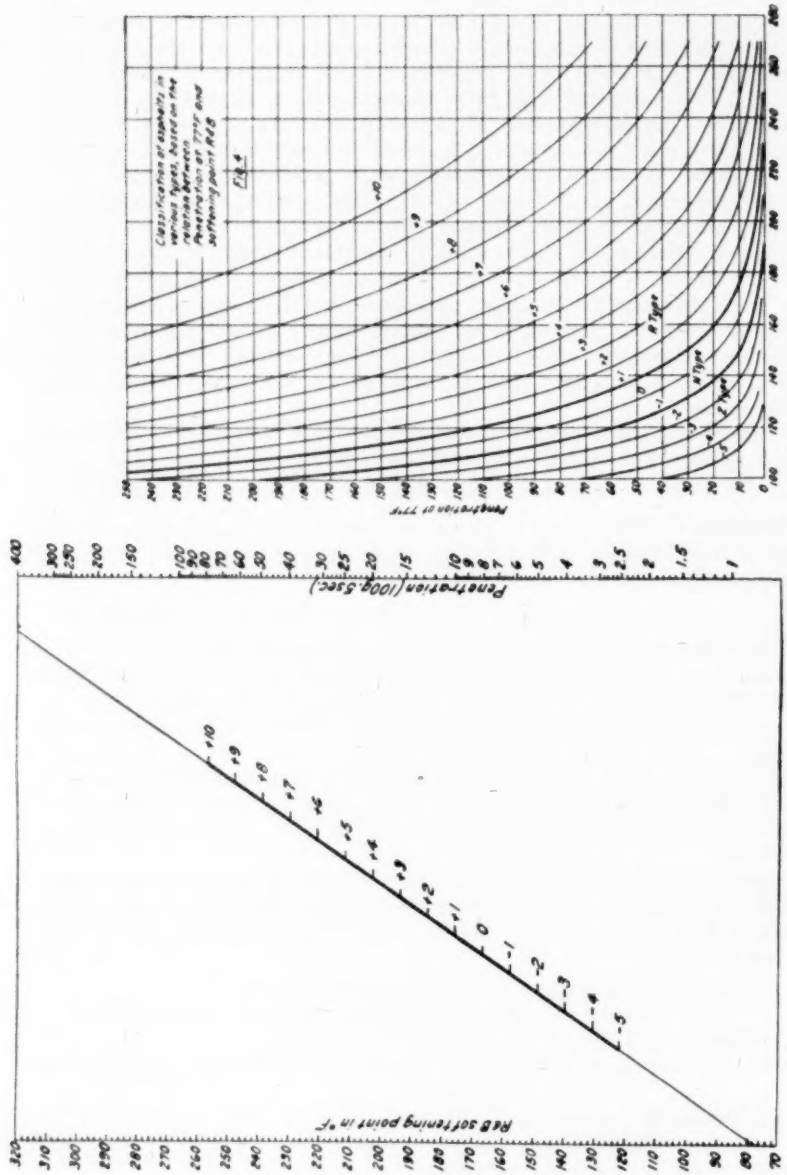

Fig 4

PFEIFFER AND VAN DOORMAAL DIAGRAMS FOR THE DETERMINATION OF PENETRATION INDEX OF ASPHALTS

It is emphasized by these workers that the foregoing grouping should be treated as a guide only, since not all steam-refined bitumens for example are of the N type, some being found in each of the other two classes.

The P.v.D. Index is critically compared in Part III of this work with certain new systems proposed in Part II by the present investigator, who

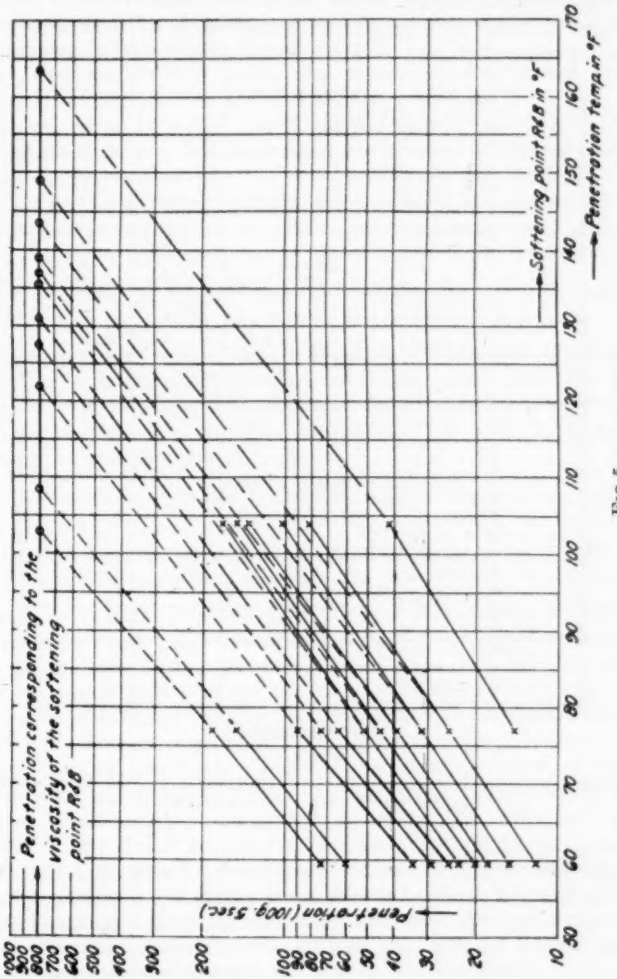
Softening point R&B in °F
Penetration temp. in °F
Penetration corresponding to the viscosity of the softening point R&B
Penetration (100g, 5sec)

FIG 5

PENETRATION-TEMPERATURE CURVES AS PLOTTED BY PFEIFFER AND VAN DOORMAAL

has made an entirely different but scientifically more logical approach to the problem on the basis of his own experimental data.

It is, however, appropriate at this stage to point out from the nature of the original assumptions that the whole theory of Pfeiffer and van Doormaal has been based on unwarranted foundations.

In the first place, the constant value of 12,000 poises assumed for the

viscosity at the softening point has already been proved to be entirely fallacious by various investigators mentioned earlier in this paper (values varying from about 5000 to 39,000 poises having been recorded). Secondly, the limitations of Saal's equation (X) have also been indicated. Thirdly, it is clear theoretically from the foregoing discussion that the penetration at the softening point cannot be 800 for all bitumens.

Reference to their own graphical presentation of their experimental results, as reproduced exactly in Fig 5, shows clearly that their contentions

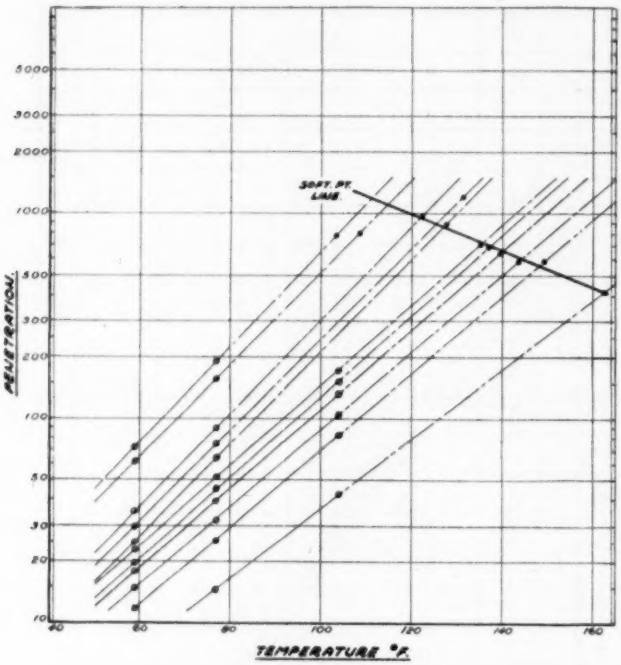

FIG 6

THE WRITER'S REPRESENTATION OF PENETRATION-TEMPERATURE DATA OBTAINED BY PFEIFFER AND VAN DOORMAAL

of the constancy of the 800 penetration value at the R and B softening-point temperature are in fact not substantiated. Using the same graphical axes, the author has depicted the identical points for comparison in Fig 6. It is evident in the first instance that insufficient penetration data have been obtained by Pfeiffer and van Doormaal to give a really accurate reflection. It is definitely dangerous to base important conclusions on only two determinations for any given line, particularly if the line has to be extended over a considerable distance to obtain further information. Reference to Fig 6 shows that the three points which do not fall on the softening point line have all been extrapolated from only two penetration points.

Nevertheless, the present author has demonstrated from Pfeiffer and van Doormaal's work—as will be shown in Part V—that there is a definite

mathematical relationship for any given series of bitumens of the same class between the penetration at the softening point and the softening point itself; in general, as the softening point increases, the corresponding penetration decreases.

It is significant that the very data which Pfeiffer and van Doormaal used in Fig 5 to illustrate that the penetration at the softening point is approximately 800 for all bitumens in fact showed variations from about 1150 down to almost 400 (see Fig 6).

Other investigators [11, 51] have also reported considerable variations, isolated values ranging from 450 to 1300 being quoted.

It is of interest to note that Lewis and Welborn [51] have confirmed experimentally that it is permissible to extend the log penetration–temperature curve to the softening point. A special needle 6 inches long but otherwise conforming to the standard specification was used, and special precautions were adopted during the testing. Excellent agreement with the theoretical values deduced by extrapolation of penetration–temperature data to the softening point was obtained.

Holmes, Collins, and Child Penetration Index (H.C.C Index)

Another approach was made by Holmes, Collins, and Child.[36] These investigators correlated penetration–softening point data for bitumens obtained from a number of sources and found that in general there is a straight-line relationship between the log of the R and B softening point and the log of the penetration. Thus :—

$$\log M = a \log P + \log K \quad . \quad . \quad . \quad \text{(XXV)}$$

or

$$M = KP^a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XXVA)}$$

where a and K are constants which depend upon the source of the bitumen and on the temperatures at which the penetrations are taken.

While this equation by itself gives no indication of the changes in consistency of any one asphalt with temperature, there is conclusive evidence that in general the higher the penetration for a definite softening point, the less the susceptibility of the bitumen to temperature change.

Two series of bitumen samples of extreme types were arbitrarily chosen as standards. The bitumen of high quality produced by vacuum distillation of heavy Mexican crude was assigned a penetration index of 100 (for all values of penetration and corresponding softening points), while the poor-quality materials representing a severely cracked tar series were given the value of 0.

A chart (Fig 7) was then prepared in which log penetration was the ordinate and the H.C.C. index the abscissa. The latter ranged in equal linear divisions from 0 to 100, and extensions were made in either direction to cater for still more extreme quality bitumens. Iso-softening-point straight lines were then plotted over regular increases of 2° F, the positions of the lines being determined by the basic-penetration–softening-point data applicable to the two arbitrary standards.

The method adopted by Holmes, Collins, and Child for their classification of bitumens was based in principle on the well-known viscosity-index system for lubricating oils developed by Dean and Davis,[17] in which a general relationship was formulated to indicate viscosity–temperature

coefficients of any oil on a scale in which the viscosity index of one series of oils having high susceptibilities was arbitrarily designated as 0, whereas that of another series possessing low-temperature coefficients was 100.

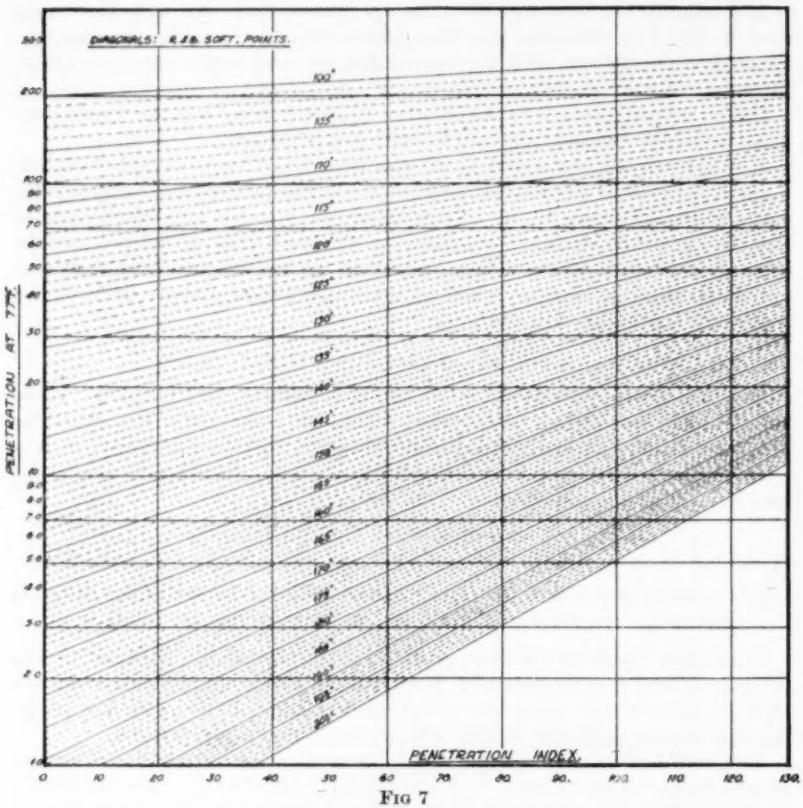

FIG 7

SOFTENING POINT–PENETRATION INDEX CHART OF HOLMES, COLLINS, AND CHILD

A critical review of the H.C.C. index in relation to the present work will also be given in Part III.

RELATIONSHIPS BETWEEN BITUMEN PENETRATIONS AT 77° F AND VISCOSITIES AT ELEVATED TEMPERATURES

Of two bitumens with the same penetration at a given temperature, the one which possesses the higher viscosity at an elevated temperature is obviously less susceptible than the other with the lower viscosity. It follows therefore that the penetration at 77° F, for example, can be linked with say Furol viscosity at 275° F to give an indication of the changes in consistency between the two temperatures.

Two recognized methods of classifying bitumens in this way have been established :—

(*a*) fluidity index of Holmes, Collins, and Child;
(*b*) fluidity factor of Zapata.

The viscosity at 275° F was chosen as the most suitable in each case, because it was found that data could conveniently be obtained at this temperature for a complete range of bitumens having consistencies varying from 200 pen at 77° F down to 20 pen. At temperatures much higher than 275° F, the differences between products from diverse sources are not very marked, particularly for the softer bitumens when the limits of accuracy obtainable by the Furol viscometer have to be taken into account.

On the other hand, at much lower temperatures, the viscosities of the harder bitumens are unduly high, with an accompanying sacrifice of experimental accuracy.

Holmes, Collins, and Child Fluidity Index

This index was also developed by Holmes, Collins, and Child [36] in essen-

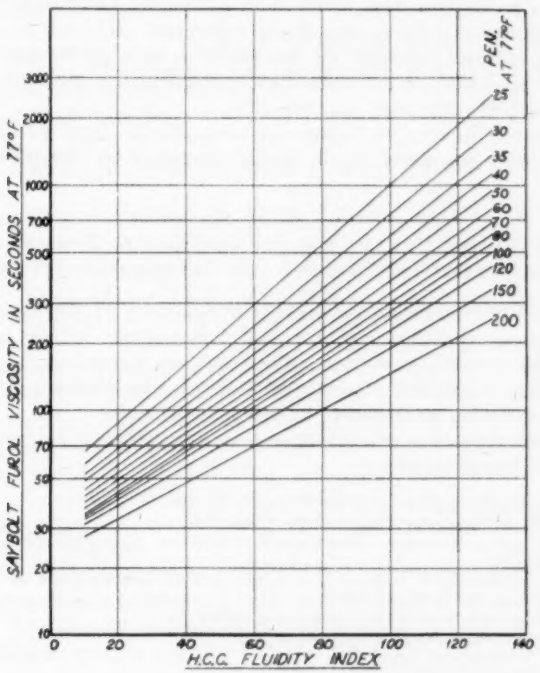

FIG 8

FLUIDITY INDEX CHART OF HOLMES, COLLINS, AND CHILD

tially the same way as their softening-point–penetration index already described.

A fluidity-index chart (Fig 8) was constructed in which the same two

series of bitumens previously used were arbitrarily assigned indices of 0 and 100 respectively. In this case, however, the logarithm of the Furol viscosity in seconds at 275° F was adopted as the ordinate in place of log penetration at 77° F as in the former chart, while iso-penetration straight lines were drawn diagonally across the chart instead of iso-viscosity lines, as a parallel to iso-softening-point lines in Fig 7. The fluidity index remained as the abscissa.

The present author has also examined the H.C.C. Fluidity Index in relation to his own experimental work in Part IV, and will further point out certain discrepancies in the construction of the chart. A revised N : H.C.C. fluidity index has been suggested to take the shortcomings into account.

Zapata Fluidity Factor

Zapata [114] has proposed the following empirical relationship to classify bitumens :—

$$\text{Fluidity Factor} = [\text{Furol viscosity @ } 275^\circ \text{ F} - \text{Pen @ } 77^\circ \text{ F}] \times \text{Pen at } 77^\circ \text{ F}/100 \quad \text{(Factor N)}$$

According to Zapata, this factor is of particular value over the range of consistencies covered by paving-grade bitumens, although he admits that it does not remain constant for materials from a given source. It was primarily introduced as a means for identifying the source of the crude oil from which the bitumen was refined.

This factor will also be compared critically in Part IV with a more rational fluidity characterization factor proposed by the present investigator.

Comparative Utility Values of Various Temperature-Susceptibility Factors and Penetration Indices

Stanfield [92] has made an interesting comparison of the more important temperature-susceptibility factors and penetration indices already discussed. The investigation was carried out on several series of bitumens prepared from a number of crude-oil sources and having a wide range of samples of differing penetration values in each series.

The factors studied and their appropriate equation or diagram references as indicated herein were :—

(*a*) Traxler and Schweyer–Asphalt Viscosity Index . . . (Factor A)
(*b*) Mitchell and Lee–Log Temperature Coefficient . . . . (Factor B)
(*c*) Nevitt and Krchma Viscosity–Temperature Susceptibility Coefficient . . . . . (Factor D)
(*d*) H.C.C. susceptibility factor involving ratio of penetrations at 77° F and 32° F respectively . . . . . (Factor G)
(*e*) Bencowitz and Boe—Index of Susceptibility . . . . (Factor J)
(*f*) H.C.C. Softening Point–Penetration Index . . . . (Fig 7)
(*g*) P.v.D. Penetration Index . . . . . (Factor M. Fig 4)
(*h*) H.C.C. Fluidity Index . . . . . (Fig 8)
(*j*) Zapata Fluidity Factor . . . . . (Factor N)

Using the index values ascertained for 100-pen bitumen as a standard reference basis in each case, Stanfield plotted the percentage deviation of each factor from the standard against the individual penetration values at 77° F for all the samples tested in each bitumen series.

It was found that, in most instances, the final numerical values of each factor depended to a large extent not only on the nature of the crude oils from which the bitumens were prepared but also upon the actual consistency of the bitumen samples tested, even though they originated from the same source and theoretically should have had identical indices of quality. In general, the results were exceedingly confusing and erratic. Indeed, in many instances, the agreement was so poor in the same series of bitumens that it was impossible even to differentiate between so-called high- and low-grade materials. The values of the factors for the hardest bitumens from any one oil were often at one extreme, while the corresponding factors for the softest materials were at the other.

The least deviation with changes in penetration was observed for the V.T.S. Coefficient of Nevitt and Krchma, while the greatest deviations were noted for the Zapata Fluidity Factor and the Index of Susceptibility of Bencowitz and Boe.

In a similar exhaustive investigation, Lewis and Welborn [51] also obtained comparative data on various indices and factors during an examination of bitumen specifications laid down by various public road administrations.

These factors included :—

1–4. The empirical factors E, F, G, and H discussed earlier and involving ratios of penetration tests carried out at two different temperatures under identical or varying conditions of loading and time.
5. P.v.D. Penetration Temperature Susceptibility . . (Equation XXIII)
6. P.v.D. Penetration Index . . . . . (Factor M; Fig 4)
7. Zapata Fluidity Factor . . . . . (Factor N)
8. Lewis and Welborn Susceptibility Factor . . . . . (Factor L)

It was clearly demonstrated that factors E, F, G, and H were unsuitable for specification purposes, four out of every five bitumens of confirmed satisfactory service being excluded. The specified minimum limits of 140 for the Zapata Fluidity Factor could also not be met in a considerable number of bitumens of proven good quality, particularly for the softer grades of material.

The conclusion was reached that none of the empirical indices, with the exception of their own factor *L*, derived directly from the log penetration–temperature curve, gave more than an approximate measure of susceptibility. The opinion was also expressed that some of the factors might be used to advantage only in controlling the uniformity of supply of material for specific jobs, but that designated limits for susceptibility factors that in fact may restrict the use of bitumens showing satisfactory behaviour in service were not rational.

A review of the results and conclusions of these two papers leaves no doubt as to the urgent necessity for more satisfactory methods of classifying bitumens. An attempt to fulfil some of these requirements has been made by the present investigator in Part II and subsequent papers of this series.

The Ductility Test

*ASTM D*113–35 : *IP* 32/42

The " ductility " of a bitumen is measured by the distance to which it will extend before breaking when the two ends of a standard-shaped

briquette specimen of the material (7·5 cm long by 1 cm thick) are pulled apart under specified conditions of temperature and speed.

The actual experimental details of the test have been rigidly standardized by the IP and by the ASTM.

The standard test temperature was formerly laid down as 77° F, but the present tendency is to specify other temperatures as well. The speed of elongation is normally 5 cm/min, but here again the use of a range of speeds has been found to be advantageous.[44, 51, 68]

The original standard IP test method specified the reporting of the highest value from three independent tests as the ductility value. This was, however, revised in 1942, and the mean result is now reported. All values should agree within 5 per cent of the mean value of three independent tests, but erratic results are sometimes encountered. A normal test is one in which the material between the two clips is pulled out progressively until the original minimum cross-section of 1 cm square is reduced to a point or thread of practically no cross-sectional area when rupture occurs.

The standard instrument is made to measure ductilities up to 100 or 110 cm, but machines with wider applicability, up to 250 cm, have been proposed by the U.S. Public Roads Administration[51, 52] and others.[11, 44] Various mechanical improvements have also been made[95] to maintain a uniform speed throughout, and to eliminate experimental disturbances such as the shock at the start of the test.

Certain Aspects of Ductility

The Effect of Temperature

Ductility cannot be possessed by completely solid bodies, nor by true liquids, but only by semi-solids and viscous liquids.

Where the bitumen is solid, therefore, as at very low temperatures, the ductility is nil. As the temperature is raised to bring the bitumen into the plastic state, the ductility increases to a maximum and then rapidly decreases to zero when the liquid condition is reached. There is a characteristic shaped curve over which the material changes from a brittle to a highly ductile plastic. The limiting temperature at which no ductility occurs is usually referred to as the " breaking " or " brittle " point.

If the ductilities of two bitumens of the same penetration at 77° F are compared at two different temperatures, it is frequently found that the one with the lower ductility at the higher temperature has a greater ductility than the other at the lower temperature. It follows that the order of ductility is thus reversed at temperatures below the point of intersection of the two ductility–temperature curves. Isolated tests at a single temperature can therefore be most misleading.

The present author has for convenience made use of the temperature at which the ductility is exactly 1 cm as one of the critical points in his work. The other critical point is the temperature at which the ductility is exactly 100. The interval between these two temperatures is an important link in the chain for assessing the rheological properties of bitumen.

Abraham [1] states that with every bituminous substance there exists a certain temperature, usually within 10° to 30° F of its Kraemer–Sarnow softening point, at which the ductility attains a maximum. In his opinion,

it is desirable that the maximum ductility should coincide as closely as possible with the average temperature to which the material is to be subjected in practice.

A similar observation has been made by Renzo,[76] who suggests that, in the evaluation of road bitumens, the ductility should be determined at certain temperatures fixed in relation to the softening point, varying from about 15° to 50° F below that value.

Broome [11], Anderson,[(discussion on 35)] and others depict ductility–temperature data graphically in a direct manner. No simple mathematical relationship is, in general, shown to be applicable to such curves. Lewis and Welborn [51] and Renzo,[76] however, have shown that ductility can be expressed reasonably as a logarithmic function increasing regularly as a straight line with rising temperature up to a point close to the maximum ductility value, where the curve changes its direction.

The present investigator also uses log ductility in his experimental work as a logical parallel to log viscosity, log penetration, and log softening point (see Part V).

Chemical Aspects

According to Spielmann and Hughes,[91] ductility in a bitumen is derived from the mixing of the oily constituents with the colloidally fine carbon discussed in Nellensteyn's theory.[64]

The paraffin wax content is of particular importance, as bitumens containing high percentages of this constituent almost invariably exhibit poor ductility characteristics.[4] McLeod [60] states that this also applies to products containing much coarse carbonaceous matter.

Holmes and Raphael [37] have investigated the effect of resins on ductility by blending various percentages with different bitumens. In general, a low resin content is shown to result in a bitumen with low ductility but with good temperature susceptibility, whilst a high resin content produces a material with relatively high ductility but poor susceptibility.

Mechanical Aspects

Abraham [1] has proposed the measurement of the cohesiveness of bitumen by attaching a tensiometer during the ductility test to give tensile strength. Evans [21] has adopted this suggestion by inserting a spring balance, reading to 100 lb, between one jaw of the ductility mould and the fixed cross-bar at the end of the machine, the other jaw being attached to the movable carriage in the usual manner.

Grant and Pullar [30] have also developed a special apparatus by which a continuous graphical record is obtained of ductility tension in grams *vs* elongation in cm. By this method Lang and Thomas [44] have found that, as a general rule, highly susceptible asphalts tend to form curves which are pointed at the maximum tensile strength and are concave in the descending portion. The maximum point is usually reached very early in the test at a ductility of about 2 cm. The areas bounded by the curves have been taken as measures of the total work done, and have normally been found to go hand in hand with maximum strength values. Exceptions to the above have, however, been noted. The method has unfortunately the

disadvantage of giving reliable results only under conditions at which the asphalts are fairly hard.

Lang and Thomas conclude that the ductility tension of an asphalt is largely a function of the viscosity.

Zichner [116] carried out cohesion measurements on binder films and binder–aggregate mixtures by determining the load required to pull apart the films or mixtures compressed between metal plates. The conclusion was reached that the fracture of binder films is generally due to other phenomena more complicated than the overcoming of cohesion. A cohesion fracture is obtained only with binders of high viscosity.

Rheological Aspects

Saal and Koens [83] have shown that ductility is related to plasticity in that bitumens of marked plasticity have lower ductilities than those which approximate to true liquids. For highly plastic bitumens, the wide parts yield less material for forming the thread than with non-plastic materials. Consequently the thread becomes thinner and breaks sooner.

Anderson (in a discussion on 35) discusses the role of elasticity in ductility. The elastic properties of a bitumen produce an elastic stretch at the beginning of the ductility test, and thereby give a certain initial ductility. As the deformation continues and flow occurs due to the viscous constituents, the elastic elements exert forces favouring the constriction of the waist, thereby weakening the briquette. Under such conditions, the bitumen has a lower ductility than if no elasticity exists. Hence elastic properties tend to increase the ductility if it is low in value, but decrease it if it is high.

This explains why highly plastic asphalts of low penetration at low temperatures have small, but definite ductilities, as contrasted with viscous materials, which break almost immediately under similar conditions. The ductilities of a given series of complex-flow asphalts may increase so gradually with increases in penetration that the values are still relatively low for penetrations at which more viscous bitumens have already reached their maximum ductility at the temperature of test.

In the case of true viscous materials small changes in penetration due to changes in the temperature of the test may be accompanied by large changes in ductility; with highly plastic and elastic bitumens the changes are gradual. Intermediate products assume intermediate positions in relation to the degree of complex flow which they exhibit.

Significance of the Ductility Test

Ductility is often regarded as a measure of the adhesive, cementitious, and binding properties of bitumens. It is probably more correct, however, to draw a parallel between ductility and cohesion, since the cohesive strength of a bitumen is independent of the nature of the aggregate with which it is associated.

Skidmore [89] and Rader [75] have each demonstrated that as the temperature in a bituminous paving mixture is reduced the strength of the composition becomes more and more dependent on the properties of the binder.

Since changes of temperature in road structures inevitably give rise to great disintegrating forces due to expansion and contraction, it is essential

for a satisfactory bituminous binder to withstand distortion under such stresses without actual rupture. The bitumen should consequently be sufficiently ductile under all conditions to prevent road failures by cracking. The importance of low-temperature ductility can therefore not be overemphasized, particularly in regions where low-temperature performance is critical.

Similarly, it is important that where a structure is subjected to vibration, the bitumen should have high ductility within the particular temperature range at which such stresses are encountered. Excessive ductility, on the other hand, is, however, undesirable from the point of view of stability.

The presence or absence of ductility in a bitumen at any given temperature is undoubtedly of more importance than the actual degree of ductility. Tests at various temperatures have special significance where road surfaces are subjected to extreme ranges of temperature.

The characteristic ductility–temperature curve of each bitumen may be used for furnishing data upon the nature, derivation, composition, and previous history of the material. It can also be of great value in indicating adaptability of the bitumen for any specific usage.

The ductility test at 77° F, as it appears in specifications, is of dubious value by itself, since the temperature of 77° F can hardly be considered to be critical in any road structure. Neither does the standard rate of pull in the test represent the conditions existing in practice at the time of failure. In fact, Zapata [115] comments that he has carried out thousands of ductility tests at 77° F without being able to establish noteworthy differences among the products tested.

Traxler and his co-workers [97, 105, 106] have shown that ductility values at various temperatures and at various rates of elongation are readily explained by the rheological properties of the bitumen under the conditions of testing. The ductility test is not regarded as a measure of consistency, because the shearing stress and rate of shear used in the test are dependent on, and vary with, the flow characteristics of the material under examination.

For almost true viscous bitumens, the speed at which the ductility test is run does not change the results appreciably, since the rate of shear has little effect on the viscosity. However, for complex bitumens with low ductilities corresponding to low penetrations at the test temperature, increases in the rate of elongation (or shear) tend to accentuate the necking effect and give even lower values.

Considerable controversy exists as to the value of the ductility test as an index of quality.

For example, Skidmore,[89, 90] Nevitt,[(discussion on 20)] and McKesson [59] all regard ductility by itself as more important, from the point of view of quality, than penetration. They agree, however, that one of the greatest drawbacks in the ductility test is in establishing a definite danger zone of values, since it is not as precise a test as penetration. Nevertheless, the importance of the test arises from the fact that ductility involves cohesion as well as hardness or consistency.

On the other hand, Lewis and Welborn [51] consider that the ductility test is not directly translatable to field performance because the bituminous binder is present in the road surfacing in thin films, the stretch of which need only be extremely short to cause failure by cracking. The ductility

test, however, usually measures extensions in terms of several centimetres. In the opinion of these workers, the penetration test is undoubtedly more significant than ductility.

Again, Endersby and his associates [19, 20] feel that the notoriously poor reproducibility of the ductility test acts in its disfavour particularly in correlations with other properties, such as durability. Penetration results, on the other hand, being far more dependable, are considered to be of greater value.

Lang and Thomas [44] and Hveem [39] also conclude that the ductility test is not very suitable for establishing any simple relationship with the performance of bitumens in service.

Broome [13] and several other workers have used the ductility test for indicating apparent brittleness in bitumens, the assumption being made that brittleness is the negation of ductility. Preston,[74] however, points out that brittleness is not necessarily the negative of ductility, since a material lacking ductility may be merely friable, fragile, or jelly-like.

Lethersich,[47] who has evaluated the ductility test for the measurement of brittleness in comparative studies involving impact and tensile strength tests, concludes that the ductility test indicates brittleness only for hard bitumens, this property being associated with low ductility (less than 1 cm) under conditions resembling the tensile-strength test. Where a bitumen is in practice subjected to a rapid rate of loading, impact tests are of the greatest importance. The tensile-strength test, which involves making measurements at a number of rates of loading, is of greater value, however, where the rate of loading is small. This test indicates a tendency towards brittleness not shown by the ductility test.

Relationship of Ductility to Penetration and Softening Point

Various workers have reported comparative data relating penetration and softening point with ductility. In some cases the experimental results have been obtained by determining the properties separately for the same sample at different temperatures. In others, work has been carried out on materials of different degrees of hardness manufactured by the same refining process from the same base material.

Lewis and his associates [49, 51, 52] have shown no consistency in the methods adopted for plotting their experimental results. For example, ductility values have been plotted directly against penetration and softening point, but irregular-shaped curves have been obtained.[51] When, however, the logarithm of the ductility has been plotted directly against the other two properties regular-shaped curves have resulted, particularly over narrow penetration or softening-point ranges.[49, 52]

So many other cases of a similar nature abound throughout the technical literature on bitumen that it is unnecessary to enumerate them. In fact, incorrect plotting of rheological data relative to bituminous substances has been, and is at present, more the rule than the exception. Such curves are illustrative only, and cannot be used for the derivation of any true mathematical relationships.

It is necessary to adopt consistent principles in the graphical representation of all such experimental data. Units of penetration, softening point,

and ductility should obviously be considered in a different category from units of length, mass, time, etc. They are, however, closely related to units of viscosity.

Thus, it has already been pointed out that a straight-line relationship is obtained—up to near the maximum ductility point—when log ductility is plotted against temperature. It has also been shown earlier in this paper that log penetration is a linear function of temperature as well as of log softening point (see equations (IX) and (XXV) respectively). Therefore it follows that the logical way of representing the relationship between ductility and the other properties is to plot :—

(*a*) log ductility *vs* log penetration;
(*b*) log ductility *vs* log softening point.

The present investigator has found the above guiding principles invaluable in his own experimental work, with the result that certain relationships have been clarified which otherwise may have remained obscure (see Part V).

It is indeed unfortunate that the importance of this point has not been fully appreciated in the past by so many other workers.

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THE NATURE OF SOAP-THICKENED LUBRICATING GREASES

By Marjorie J. Vold * and Robert D. Vold *

Summary

Phase diagrams have been determined for calcium stearate and its hydrate, and lithium stearate, in cetane and in decalin, and the system sodium stearate–cetane.

It has been demonstrated that grease systems of apparently similar phase condition may differ from each other in properties such as X-ray-diffraction pattern, liquid loss under pressure, yield value, effect on rubbing surfaces, etc. This is attributed to the existence of a definite type of organization or structure of the dispersed soap particles, a hypothesis which appears to be confirmed by electron micrographs of grease.

The paper summarizes the general results obtained in the authors' laboratory in a continuing programme of study of the properties of colloidal solids, with particular reference to greases, in which the structure-determining component is a soap. This work was supported in part by the U.S. Office of Naval Research (Contract No. N6-onr-238-TO 2, NRO57057) for three and a half years. More detailed discussion of each of the topics here briefly considered may be found in the various Technical Reports submitted to the Office of Naval Research[12–16] and available on loan from the Library of Congress.

Practical Problems

A grease is a lubricant which has been thickened in order that it remain in contact with the moving surfaces and not leak out under gravity or centrifugal action, or be squeezed out under pressure. Thus a major practical problem is the provision of a structure which will stand up under shear, and at all temperatures to which it may be subjected during use. At the same time the grease must be able to flow into the bearing through " grease guns " and from spot to spot in the lubricated machine as needed, and must not of itself add significantly to the power required to operate the machine, particularly at its start. This is an exacting set of rheological requirements.

During use, a grease is subject to chemical changes, primarily oxidation. Thus a means must be found to minimize oxidation or the effect of its products on the grease. Another source of breakdown is exposure of the grease to water or steam, which must also be controlled. Storage stability with respect to retention of rheological properties as well as gross syneresis is also a problem.

Finally, grease systems display a tremendous and seemingly erratic sensitivity in properties to superficially minor alterations in manufacturing operations, and unavoidable and often unspecifiable variations in raw

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materials may require modification in compounding procedures ascertainable only by trial and error on a plant scale.

Grease research, like many other investigations of technically important systems, has two aspects: the exercise of whatever combination of insight and intuition may be brought to bear on solution of a current pressing problem, and the slower but eventually more significant development of basic understanding of why these systems behave as they do.

Fundamental Problems

In the study of greases the question "what" must be answered before the question "why" can be so formulated as to direct intelligent search for its answer. What is the structure of a soap-thickened oil? Has the soap dissolved in the oil, or the oil in the soap, or is there only a mechanical dispersion, or is there a more elaborate soap structure not aptly described as a mere dispersion? How does this answer depend on such variables as temperature, gross composition, pressure, mechanical processing, minor constituents? How does it depend on past history of the system and on time? What is the mechanism by which the structure becomes established during manufacture and by which it is changed during use under varied conditions? These are the present problems, to which partial answers may now be given.

Fortified with some basis for the hypothesis that the soap molecules are integrated into a colloidal structure comprising an irregular porous clumping of imperfect crystallites; it is becoming feasible to ask why this structure should result from the packing characteristics of the individual molecules.

Phase Diagrams and Phase Maps

A phase map of a system is a plot of temperature versus composition which shows the number and nature of the phases present at each point. It is thus a concise and informative means of describing the system. For systems which are in a state of equilibrium dependent only on temperature and composition, application of the phase rule to the map, which is then the equilibrium-phase diagram, can yield a great deal more additional useful information, such as the composition of each phase and its relative amount in multi-phase regions, and the nature of the changes which occur as composition or temperature is varied.

For soap systems, two sorts of maps have proved useful. Equilibrium-type diagrams have been determined for a number of systems, even though it is likely that the solid phase is not necessarily the most stable thermodynamically. Moreover, the "equilibria" specified are attained only slowly except at high temperatures. These diagrams are useful in so far as the actual physical state of the system at room temperature, including rheological properties, may depend on the phase state at the temperature and composition at which the initial dispersion of soap in oil is prepared. They also predict the ultimate state at elevated temperatures when the grease is in use, and serve as a guide to the changes that may occur in lubricant films. In this latter case the phase behaviour suggested is that

of the solvent-free soap somewhat modified by adsorption forces at the surface of the metal.

Phase maps which give the room-temperature state as a function of temperature and composition after extensive mechanical working have proved very useful for soap–water systems,[1] and a beginning has been made for their extension to soap–oil systems.[22]

Phase Diagrams of Soap–Oil Systems

For calcium stearate,[15] calcium stearate hydrate,[15] anhydrous sodium stearate,[4, 7, 9] and lithium stearate [11, 12] in the two pure hydrocarbons, *n*-hexadecane (cetane) and decahydronaphthalene (decalin, *cis–trans* mixture) the soaps display only exceedingly minute solubility at temperatures up to above 100° C. Dilute suspensions remain turbid or, after heating to transparency, become turbid again on long standing. Similar behaviour is observed with petroleum oils, the concentration of soap soluble in the bulk oil at room temperature being minute.

The gross features of the X-ray-diffraction patterns of greases at room temperature are those of the soap plus the oil in additive relation. Likewise, polymorphic transitions of the soap can be observed also in the grease, for example, by thermal analysis, up to above 100° C.

From these facts it may be concluded that the thickening and rheological behaviour at lower temperatures are explicable in terms of formation of aggregates of unreacted soap crystallites rather than to swelling of the soap in the oil.

The solubility of soap in oily solvents increases rapidly over a temperature region which depends on the soap and the solvent but more critically on the soap. All of the soaps so far investigated display a sequence of mesomorphic (liquid crystalline) forms when the solvent-free soap is heated. The phenomenal increase in solubility seems generally associated with the formation of one of these. For example, calcium stearate begins to dissolve at about 120° C, sodium stearate at about 160° C, lithium stearate at about 180° C, etc. Systems containing the dissolved soap are generally highly viscous in the absence of additives, and do not have grease texture to any marked degree. Extension of the useful temperature range of greases to higher temperatures thus demands, among other things, raising the temperature attainable before the soap dissolves either by choice of soap or oil or by addition of a third component.

At sufficiently high temperatures sodium and lithium soaps are soluble in all proportions in cetane and in decalin to form an isotropic liquid solution, but this is not true for calcium stearate (at least up to 250° C, for at this temperature samples containing from 60 to 90 per cent soap are still brilliantly anisotropic).

This completes the description of what is accepted as unambiguously proved about the phase behaviour of soap–oil systems. Much remains to be learned in the region of temperature within which the soap is partially soluble and the undissolved portion has imbibed some solvent and is in a liquid crystalline or mesomorphic state. This region is important because in it are existent the nuclei from which grow the solid crystallites of the ultimate grease. It is difficult to study, because the phase state of a given

sample is not apparent on visual examination, and because changes in physical properties such as heat content, vapour pressure, and specific volume between mesomorphic phases are notoriously small.

The simplest conceivable behaviour would consist in each of the known mesomorphic forms of solvent-free soap co-existing with liquid solution within its own temperature range of existence. Available data for lithium stearate in cetane and in decalin, and calcium stearate and its hydrate in cetane and in decalin cannot be reconciled with this hypothesis. The same is possibly true of sodium stearate, although in this case quite divergent results have been obtained depending on the presence or absence of traces of moisture.[9]

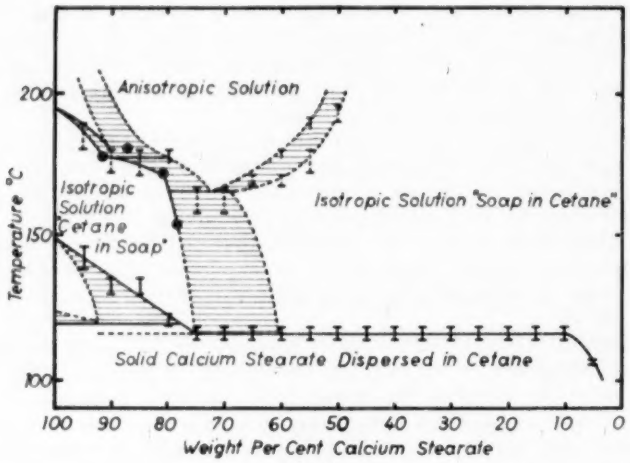


FIG 1

PHASE MAP OF THE SYSTEM CALCIUM STEARATE–CETANE. THE MAP IS CONSISTENT WITH THE REQUIREMENTS FOR AN EQUILIBRIUM PHASE DIAGRAM. I-SHAPED POINTS, TEMPERATURE REGIONS WITHIN WHICH VISIBLE CHANGES IN PHASE OCCUR. DEFINITIVE RESULTS OBTAINED BY DIFFERENTIAL CALORIMETRY.

The data consist of sets of curves of composition versus temperature at which discontinuous changes in physical properties can be observed. These include visually apparent changes such as separation of a second phase from isotropic liquid on cooling, disappearance of solid on heating, development of birefringence, etc., and also changes in heat content observed as peaks in curves of temperature difference versus time when the sample and an inert reference material are heated in the same thermal environment (differential calorimetry). These are taken as evidence for the presence of phase boundaries at those temperatures, and the nature of the regions which they bound are determined by application of the phase rule.

On this basis it seems likely that soap and oil together can exist in types of mesomorphic states not found for the solvent-free soap, and diagrams such as Fig 1 have been obtained. Moreover, the methods have been developed for determination of similar diagrams for other systems of the same type. The next question is as to the uses to which they can be put in

relation to the study of grease systems which exist only in temperature and composition regions characterized as consisting of solid crystallites and almost soap-free solvent.

Modifications of Solid Soaps

Oil-free sodium and calcium soaps can exist in a number of different modifications at room temperature. This point has not been investigated for lithium soaps. These modifications differ conspicuously in their X-ray-diffraction patterns, although in no case except α sodium stearate hemihydrate have single crystals been prepared adequate for determination of the space group. The several forms do not appear to differ greatly in thermodynamic stability, and spontaneous transformation to the most stable does not occur readily.

It has been found that laundry and toilet soaps containing 15 to 30 per cent water differ conspicuously in physical properties such as texture, lathering rate, age hardening, resistance to water penetration, etc., depending on which of the sodium-soap modifications is present.[6, 19] For the sodium-soap greases so far examined, only one of the possible forms has been found (σ).[10] This is because the only conditions known for realization of most of the others involve mechanical agitation in the presence of water. The possibility of preparing oil dispersions of these other forms has not been explored, and is an inviting field for further work.

Four modifications have been found for anhydrous calcium soaps, and designated as VI A, VI H, VI N, and VI S.[20, 21] Roman VI comes from numbering the known allotropic forms appearing successively on cooling the melt, although possibly there may be other still unidentified forms existing between room temperature and the melting point. VI A appears to be the stable form of the anhydrous soap, and VI H, a structure similar to that of the monohydrate. The designations VI N and VI S are somewhat adventitious. VI N is realized on dehydrating some hydrate samples and on quick cooling of concentrated soap–oil systems. It is tentatively regarded as consisting of randomly stacked slabs each containing parallel calcium stearate molecules in roughly hexagonal close packing with their long axes not far from perpendicular to the face of the slab. VI S is formed by slowly cooling systems containing calcium stearate and both water and cetane from about 155° C. It can be converted to VI H by mechanical agitation in the presence of cetane, and is currently believed to differ from VI H only in the type of packing together of the same sort of slabs or ordered two-dimensional crystalline layers. Fig 2 shows typical diffraction patterns of the four modifications.

Systems of hydrous calcium stearate in cetane and other oily solvents having grease-like properties show VI H or VI N diffraction patterns. Samples subjected to varying thermal history display pattern differences which are outside experimental error but still not sufficient to warrant supposing the existence of a further multiplicity of forms. Attempts to correlate physical properties of the systems, such as curves of yield value versus composition with these variations in X-ray pattern, have been unsuccessful. This is also the case even when very gross differences in diffraction pattern are induced, as can be done with small amounts of added

stearic acid, from which it can be concluded that these properties are controlled primarily not by which phase is present but by the interaction of the primary particles to form colloidal structures.

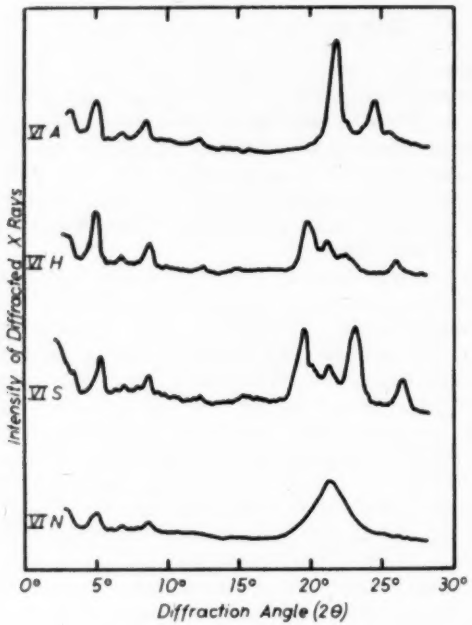


FIG 2

CHARACTERISTIC DIFFRACTION PATTERNS OF FOUR MODIFICATIONS OF ANHYDROUS CALCIUM STEARATE

LIQUID LOSS UNDER PRESSURE

When samples of gels of calcium stearate in cetane are compressed, liquid is exuded, at first rapidly and then more slowly, until a limit is reached at which no more cetane can flow out at the given pressure.[3] A similar behaviour for commercial greases is described by Farrington and Humphreys.[5]

The rate and amount of liquid loss, and also the final composition of the system, depend on the total soap content and also critically on the content of third components (as water), of which a substantial number have been investigated. The extent and rate of liquid loss decreases markedly when the soap content exceeds about 17·5 to 18 per cent calcium stearate hydrate in cetane. The ratio one mole of water per mole of soap is optimal for stability against liquid loss under pressure. However, methanol and stearic acid both also increase the stability of systems of calcium stearate in cetane, and in neither case does the composition of maximum stability correspond to any simple mole ratio.

Additives which increase the stability of systems of calcium stearate in

cetane appear, without exception, also to lower the viscosity of the samples at the relatively elevated temperatures (155° C) at which the soap was dispersed. They are all materials which could enter into hydrogen bonding or form association complexes with calcium ion (water, alcohols, amines, glycols, fatty acids, etc.).

Exudation of liquid under the given experimental condition can be thought of as filtration of the liquid through a mat of continually diminishing porosity. The actual porosity of any particular sample can readily be supposed to depend on the manner of its preparation. Thus additives forming a complex with calcium ion may " block " crystal growth, or they may block it in only certain directions, leading to development of strongly anisometric particles. These suggestions are, however, as yet purely speculative.

Yield Values

In contrast with liquid loss under pressure, the yield values [2] of systems of calcium stearate hydrate in cetane increase monotonically with in-

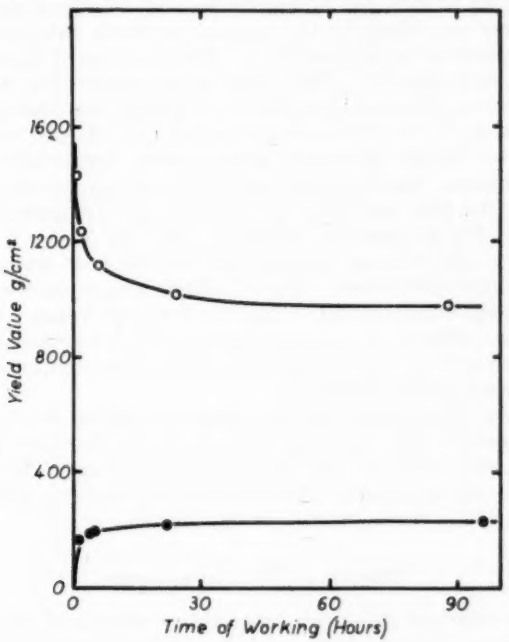


Fig 3

YIELD VALUES OF SYSTEMS OF CALCIUM STEARATE MONOHYDRATE (45 PER CENT) IN CETANE (55 PER CENT). TOP CURVE IS FOR A SAMPLE QUENCHED AFTER EQUILIBRATION AT 155° C. BOTTOM CURVE IS FOR A SAMPLE COOLED SLOWLY AFTER EQUILIBRATION AT 155° C.

creasing soap content. No evidence of any inflection near 17½ to 18 per cent soap was found. The same additives which increase the yield value

decrease the liquid loss (so far as has been studied), but a given additive concentration is not equally effective on the two properties. Thus for water the highest yield value occurs for about one-half mole per mole of soap rather than at the composition of the monohydrate, which gave the maximum pressure stability.

With mechanical working, the yield value of quenched-gel systems diminishes, rapidly at first and then more slowly, reaching a limit after about 30,000 strokes (for a 45 per cent soap system). A slow-cooled 45 per cent system is a relatively unstable, syneretic quasi-gel, resembling somewhat a mechanical dispersion of calcium stearate in cetane at room temperature. Such a system displays an increasing yield value with increasing time of working, again approaching a limiting value, but far below that of the worked system prepared by high-temperature dispersion of the soap. Exemplary data are given in Fig 3.

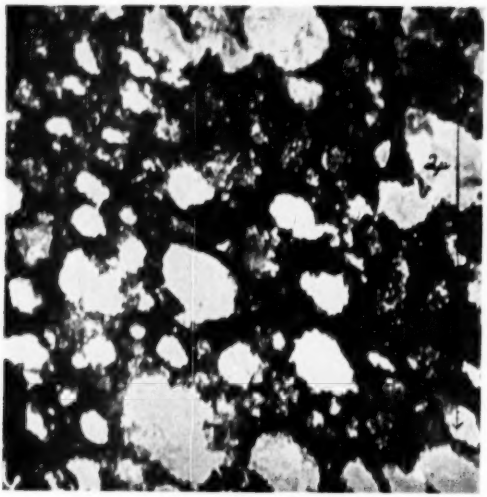
Colloidal Structure

It is likely, or at least not unreasonable, that the rheological properties of a grease are controlled by the manner in which the soap particles it contains are grown or packed together. This is a type of structure which is not easy to study directly. The electron microscope has entirely usable resolving power, but conventional means of sample preparation—spreading the grease on to a thin film and extracting the oil with solvents—seem guaranteed to disrupt whatever inter-particle organization may have existed. Recourse was therefore had to the slicing technique developed by others for use with biological specimens to prepare grease slices 0·05 to 0·1μ thick.[17] Fig 4 shows two of these. Fig 4(*a*) shows a sample containing 45 per cent calcium stearate and 1·17 per cent water (soap basis) which has a high yield value. Fig 4(*b*) shows a vigorously worked sample with 2·9 per cent water having a relatively low yield value. It is apparent that these also differ in the amount and texture of a sponge-like structure which is thought to be basic to the generation of grease-like properties in a calcium stearate–cetane system.[18]

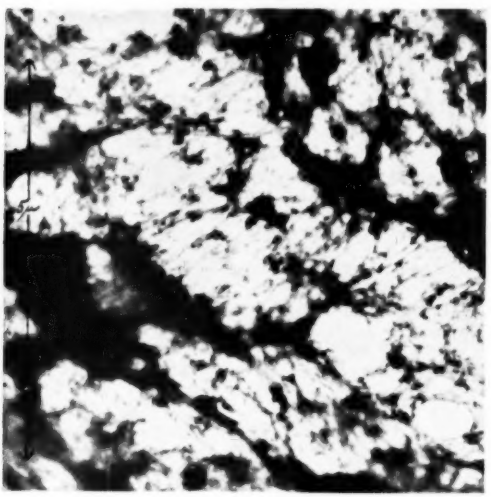
Pores such as are shown in Fig 4(*a*) filled with cetane would be expected to have a somewhat different total electron density than does the surrounding soap matrix. This should result in a scattering of X-rays at small angles to the incident beam. This affords a promising field for further investigation of the characteristics of this structure.

Friction and Lubrication

That soap dissolved in oil can lower the coefficient of friction between rubbing surfaces appreciably more than oil alone is well known, and has been ascribed to the formation of a soap film on the surfaces. With very dilute dispersions of soaps in cetane, studied at low loads in the Shell four-ball wear machine, small breaks were obtained in curves of coefficient of friction versus temperature at temperatures corresponding to polymorphic transitions of the soap. The apparent conclusion that the adsorbed films show the same phase transitions as the bulk material may, however, be fallacious. For example, the protective film may be formed by mechanical



A. 45 PER CENT SOAP, 1·17 PER CENT WATER (SOAP BASIS); WORKED TWENTY STROKES; YIELD VALUE 3400 G/SQ. CM.



B. 45 PER CENT SOAP, 2·9 PER CENT WATER (SOAP BASIS); WORKED 130,000 STROKES; AGED THREE MONTHS; YIELD VALUE *ca* 600 G/SQ. CM.

FIG 4

ELECTRON MICROGRAPHS OF GELS OF CALCIUM STEARATE IN CETANE

[*To face p* 165.

rolling out of soap crystallites rather than by adsorption, with one crystalline form softer than the other. Alternatively, at low loads and high speeds shear may occur at some point in an adsorbed multilayer where the structure is that of the bulk crystallite, even though the underlying primary monolayer may have a different structure and a different transition temperature. At high pressures and slow speeds the friction increases continuously with increasing temperature with no breaks corresponding to the transition temperatures of the soap. This may be explicable either in terms of the added pressure resulting in forcing the opposing metal surfaces together except for an adsorbed monolayer with properties differing from the bulk soap, or from the reduced viscous drag not pulling in sufficient crystallites between the rubbing surfaces to provide lubrication.

Some authors have suggested that a grease functions in lubrication only as a storehouse for oil. This has not been proved, but even if so, the " oil " exuded will contain traces of soap in suspension or even solution which are sufficient to produce a substantial reduction in friction and a moderate extension of the severity of operating conditions which can be tolerated.

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THE DETERIORATION OF TRANSFORMER OIL

PART I. OPERATING DIFFICULTIES AND THEIR CAUSES

By L. Massey

Summary

The functions of oil in a transformer and the operating conditions are briefly described. The manifestations of deterioration obvious to the operating engineer are related to the chemical factors involved, and the requirements for limiting oil deterioration are discussed. The necessity of accelerated laboratory tests for evaluating the oil and the materials of construction of a transformer is emphasized.

The Functions of Oil in a Transformer

The principal purpose of this paper is to discuss some laboratory tests concerned with the selection and performance of transformer oil, but for the information of those not familiar with the engineering aspects of trans-

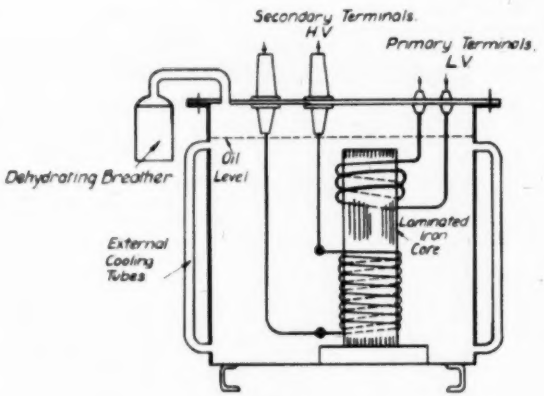

Fig 1

ESSENTIAL FEATURES OF VENTILATED TYPE TRANSFORMER

former practice some introductory remarks are made describing the nature and function of a power transformer and the reasons governing the use of oil.

A transformer consists essentially of two copper coils wound on a core of laminated iron (Fig 1). Its function is to transform electricity from one voltage to another, the transformation ratio being very nearly the same as the turns ratio. Transformers vary in size from the tiny audio-frequency transformers used in domestic radio sets to very large power transformers weighing more than 100 tons used for transforming from the very high voltage at which electricity is now transmitted to low voltages suitable for the operation of domestic and industrial equipment.

During the operation of a transformer two features are related to the use of oil—the presence of high electrical stresses and the development of heat.

In smaller transformers these features may be catered for by direct heat radiation from the coil and core and by the choice of solid insulants, but in large power transformers the very high stresses and the large amount of heat developed create special difficulties. For example, the presence of air-filled spaces in fibrous insulation and between charged metal conductors greatly limits the breakdown voltage, and the amount of heat generated in the coils of these transformers is sufficient to raise them to very high temperatures. It is in these power transformers that oil is used as an insulant and heat-transfer medium.

The electric strength of a material is influenced by many factors such as the geometry of the electrodes and the form of the applied voltage, but as a rough indication the breakdown voltage of air across a 4-mm gap is 10 kV, and that of oil across the same gap is 60 kV. It is therefore obvious that by immersing the coil in oil the physical magnitude of the spacing between adjacent conductors or between winding and core can be materially reduced, and that the breakdown voltage of fibrous insulation can be greatly increased. The presence of moisture in a coil also affects its electrical properties. Oil immersion seals the coil from direct contact with atmospheric moisture.

As the coil has already been immersed in oil for insulation purposes, it is obviously convenient to use the oil for heat dissipation by arranging that it shall circulate over the coil and then to heat-radiating surfaces. In the simplest form the coil is suspended in a plain metal oil-filled tank. In the next stage radiator tubes are fitted to the tank to increase radiation area and to promote thermal circulation. Obvious developments, as the load increases, are to provide pump circulation and water cooling for the oil.

Whatever the detail features of construction, the important point in so far as the life of the oil is concerned is that it is raised in temperature and kept in constant circulation.

The two essential functions of transformer oils are therefore to provide a fluid dielectric medium and a heat-transfer medium.

New oil as now supplied is fairly satisfactory in both respects. Hydrocarbon oils as a class possess high intrinsic electric strength, high resistance, and low power factor. The transformer engineer concerns himself only with electric strength (usually expressed as breakdown voltage—B.D.V.) and is satisfied with a value of 60 kV which can be obtained with bulk consignments.

As a heat-transfer medium the properties called for are low viscosity, low freeze-point, high specific heat, and non-corrosive nature. New oil is chemically inert, and present oils freeze below -30° C, giving an ample margin for service in the U.K. A lower viscosity might be preferable, but this is limited by the flash point. In America lower viscosity oils are used, but lower flash points are accepted than would be considered desirable in the U.K. A high specific heat would be an advantage, but this is a fundamental property, and nothing can be done on this score.

Apart from purely technical considerations, there is no alternative liquid available which offers a reasonable combination of properties at a price which can compare with that of transformer oil.

Practical Manifestations of Oil Deterioration

Oils deteriorate in service for reasons which will be discussed later. The practical and harmful manifestations of this deterioration obvious to the engineer are as follows :—

(i) a decrease in the electrical breakdown strength of the oil caused mainly by the presence of moisture and fibres;

(ii) the formation of solid sludge which deposits on the coil and in the circulation ducts, thereby hindering heat dissipation;

(iii) the formation of acidic products which show their presence by the corrosion of metal parts and the embrittlement of cellulosic insulation.

In addition to these harmful products, a deteriorated oil generally darkens in colour and develops a characteristic smell.

Electric strength of an oil can generally be maintained at a satisfactory value by simple treatments such as filtering and drying. A sludged-up transformer calls for very careful treatment, and may even require a major overhaul. Acidity formation can be of importance in itself if the oil acidity rises to very high values, as occurs particularly with highly refined non-sludging acid-forming oils. (Direct damage from acidity is, in fact, practically confined to transformers filled with Class A oil.) Acidity, however, has an importance at low values, at which it causes little direct damage, because it serves as an index to the stage of oxidation of the oil, for it is impossible to obtain from a transformer samples of oil containing a truly representative proportion of sludge.

Another type of deterioration is the formation of carbon, hydrogen, and hydrocarbon gases due to arcing and similar electrical faults. The cause may be the presence of the deleterious compounds indicated above, in which case the arcing is a secondary cause of failure. On the other hand, the arcing may be caused by mechanical failure or electrical surges, in which case it is not associated with the chemical failure of the oil. This type of failure is not discussed in this paper.

In the great majority of transformers the deterioration of the properties occurs very slowly and progressively over a large number of years, but in a very small minority of cases severe failure takes place in short periods.

The cause of severe failure is often obscure. It is, for instance, well known that two transformers may be built side by side, filled with oil from the same consignment and put in commission side by side on the same load and that, during service, oil in one will deteriorate at a different rate from that in the other. The least deterioration occurs in large transformers located in big power-stations. The worst deterioration occurs in small transformers located in small sub-stations or on private premises. The reasons for the difference in behaviour forms one of the subjects of this paper.

It must be emphasized that although the instances of severe breakdown are a fraction of 1 per cent, they cause a disproportionate amount of trouble, for to take a transformer out of commission for reconditioning may interrupt a vital service and cause severe loss and inconvenience to the owner and unpleasant repercussions on the suppliers of the oil and transformer.

Factors Influencing Oil Deterioration

It can be accepted as axiomatic that, if a transformer oil is sealed in an inert container in the absence of oxygen at temperatures not exceeding 120° C, it will remain unchanged almost indefinitely.

It follows that changes in properties in service are the result of contact with other materials. The possibilities fall under two headings :—

(i) contact with the atmosphere;
(ii) contact with materials of construction of the transformer.

These are not only theoretical possibilities but proved factors in oil deterioration.

Contact with Atmosphere

Two major influences are exerted by the atmosphere, the first by moisture and the second by oxygen. There are other possibilities, such as the location of the transformer in an atmosphere containing impurities (*e.g.*, chemical fumes or high dust concentrations), but these are special cases.

Effect of Moisture. Oil exposed to the atmosphere picks up moisture by direct absorption, but a more important source of contamination is that caused by atmospheric condensation on the internal metal surfaces of ventilated transformers. The primary effect of this water in the presence of other contaminants is to decrease the electric strength of the oil, but its presence is harmful in other ways. It makes the organic acidity present very much more active than when dry and promotes corrosive attack on metals and cellulosic materials. Sometimes it is also claimed that it accelerates oil oxidation.[1, 6]

Oil at 20° C dissolves about 50 parts of water per million, and this amount has been shown to reduce the B.D.V. of an oil by about 20 per cent as compared with commercially dry oil. Increase in concentration above this saturation value causes only a negligible further decrease in B.D.V.[2]

Dry fibres in a dry oil also reduce the B.D.V. by about 20 per cent, but the joint presence of 50 parts of water and less than 1 part of cotton fibres per million of oil has been shown to reduce the B.D.V. by up to 90 per cent.[3] The reason for this is that the damp fibres tend to be attracted to regions of high stress, where they line up, shorting the gap. Fibre length is obviously a factor.

In general, any suspended impurity will emphasize the effect of water on B.D.V.; that is, they assist particles of water to remain in suspension in the oil, in which condition water has a far greater influence on B.D.V. than it has when dissolved in the oil. However, as all transformers contain fibrous insulation, fibres are likely to be the major factor.

These figures possibly explain the fact that transformers containing water separated at the bottom are sometimes encountered in which the oil B.D.V. is reasonably high. It is to be assumed that in these cases the oil is free from fibres and that the small decrease in the B.D.V. due to pure water is well within the factor of safety of the transformer.

These facts also have a bearing on other troubles, *e.g.*, the difficulty of oil suppliers in keeping new oils up to the required B.D.V., the need for thorough drying out of the fibrous insulation before oil is introduced, and

the risks associated with gross water contamination when it settles on the insulation instead of sinking to the bottom, in which latter case it is much less harmful.

The effect of water and fibres on the B.D.V. is typical of many of the deterioration changes, *i.e.*, that very small quantities of contaminants can produce major changes in the desirable properties of an oil.

Effect of oxygen. The second major influence of the atmosphere is contact with oxygen. All petroleum oils combine to some extent with oxygen. The products of this oxidation are very complex. From the practical viewpoint they can be classed as water; volatile gases such as CO_2, low-molecular-weight acids, aldehydes, and the like; oil-soluble compounds, particularly the organic acids and organic peroxides; and solid sludge.

The water of oxidation supplements that which has been picked up from the atmosphere.

The organic acids may condense on the metal parts of the transformer above the oil level, causing corrosion, or they may remain dissolved in the oil, causing its acid value to rise and the fibrous insulation to be embrittled. Peroxides are also known to embrittle fibrous insulation. This leads to an increase in loose suspended fibres in the oil, which in turn affects the value of the breakdown voltage. The solid sludge settles on the coil and in the ducts. As these are major difficulties encountered in transformers the importance of oxidation is apparent.

For a given oxygen access the rate of oxidation in a transformer is influenced by two factors—oil temperature and the presence of catalysts.

There are three cases which can be recognized for temperature conditions during transformer operation :—

(i) normal continuous operation within the manufacturer's loading recommendations;

(ii) very short-period conditions due to accidental short-circuits or lightning discharges;

(iii) continuous operation above the recommended loading.

The temperatures attained during normal service are limited by the designer on the basis of the satisfactory life of the solid and fibrous insulation present. For Class A insulation * temperatures up to 105° to 115° C are permissible, and the maximum copper temperature is therefore never allowed to exceed 115° C. Taking into account various factors, such as permissible short-period overloads, this maximum copper temperature corresponds to a maximum peak bulk-oil temperature of 90° C and a maximum maintained bulk-oil temperature of 85° C.

In practice, owing to the occurrence of peak loads for only short periods and the need for a reasonable factor of safety, the oil for the greater part of its working life has a temperature ranging from 50° to 80° C. In fact, it is

* Insulating materials are classified in the following way :—

Class 0. Cotton, silk, paper, and similar organic materials when neither impregnated nor immersed in oil.

Class A. Class 0 materials when impregnated or immersed in oil.

Class B. Mica, asbestos, and similar inorganic materials in built-up form combined with a binding cement.

Class C. Mica without binding cement, porcelain, glass, quartz, and similar materials.

probable that a very large number of power transformers operate at a bulk-oil temperature of about 60° C. During normal working, however, there are thin films of oil in direct contact with copper which can reach the maximum copper temperature of 115° C.

Accidental short-circuits cause the copper to reach much higher temperatures, but as this is only for very short periods the effect on bulk-oil temperature is negligible. The permitted copper temperature under these conditions is 250° C,[4] but for electrical reasons it is extremely unlikely that in practice the copper will reach more than about 150° C. This does mean, however, that thin films of oils may reach 150° C.

The importance of these thin films of oil reaching these high temperatures is debatable. The actual amount of oxidation products must be very small relative to the main oil bulk, but traces of catalysts formed may disproportionately effect the oil bulk.

The third case, that of gross overloading of a transformer, may be forced on an electricity-supply authority by the present abnormal conditions, in which case there is an accepted loss of life, both for the fibrous insulating materials and the oil.[5] On the other hand, in small private concerns overloading may occur due to ignorance of the results. In both these cases the temperature limits depend on the circumstances.

Contact with Materials of Construction of Transformer

The second contributory factor in oil deterioration is contact with the materials of construction. A wide range of materials is used in a transformer. The core is built up of sheets of silicon iron. These sheets are insulated from each other by either paper or enamel. If paper is used it is stuck on by an adhesive, frequently starch or flour paste. The coils themselves are of copper, insulated either with cotton or paper, and may be wrapped with cotton, linen, glass, or asbestos tapes, which in turn may be plain or varnish treated. Pressboard and presspaper are used to support the coils, and very thick sizes of pressboard are cemented together with an adhesive. Wooden blocks are also used as supports. The coils themselves may be varnish impregnated. Leads are soldered together, and nuts and bolts of steel, possibly nickel or cadmium plated, are also present. The container tank is of mild steel, and may possibly be varnished to resist corrosion. The lid is probably varnished or painted for the same reason, and is gasketed with any one of several different gasket materials. Then the terminals are encased in phenol-formaldehyde resin-bonded paper tubes, and possibly phenolic or other mouldings and laminates are used for various purposes. In each class of material wide variations in composition are possible and, in addition, the properties may be altered by the processing which they have received and by the presence of impurities.

To choose and control these materials so that they have no influence on an oil is a formidable task. It is probably true to say that this selection has been carried to the point at which no gross contamination is permitted, but that contamination by traces of some of these materials occurs. In some cases these traces are harmless, but in others complex factors are involved usually linked up with the oxidation reactions.

These catalytic effects of materials are not yet fully understood.

Methods of Limiting Deterioration

To minimize oil deterioration in transformers it will be clear that there are three requirements :—

(i) the oil must be protected against contact with the atmosphere;
(ii) materials of transformer construction must be inert towards oil, particularly with respect to their ability to catalyse oxidation;
(iii) oils of maximum stability must be chosen.

The first requirement is one of mechanical design. The sealing of transformers against the atmosphere is an accepted practice, particularly for large transformers. The difficulties lie in taking care of the thermal expansion of the oil and of the explosion hazards. The most common form of expansion device is the conservator, which is a small chamber fitted above and connected to the main tank (Fig 2). In this chamber the rising

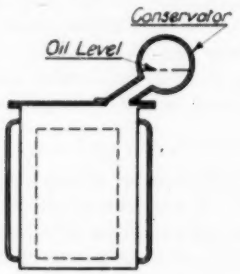

Fig 2

CONSERVATOR TYPE TRANSFORMER

and falling oil level exposes only a small surface to the air. In addition to this partial sealing device, many other mechanical devices are used or have been proposed for complete sealing, but they find less favour in the U.K. than the conservator.

Oil performance in these conservator-type transformers is almost invariably satisfactory. This is certainly largely due to the limitation of contact with atmosphere, but the situation is a little obscured by the fact that conservator transformers are generally of a large size and are located in large power-stations where they receive adequate maintenance attention.

Unfortunately, however, circumstances prevent the sealing of many smaller transformers. There are a large number in service requiring maintenance and, for various reasons, open transformers must still be manufactured. These are fitted with lids, but there is an air space above the oil, and breathing vents are necessary. As stated earlier, it is in this class of transformers, usually operating in small sub-stations and private premises, that oil troubles are experienced.

Both in conservator and ventilated-type transformers the use of dehydrator breathers is common practice, and is obviously desirable. The trouble here is again that they are not always serviced as frequently as they should be. " Gadgets " of any type are looked on with disfavour by the engineer.

While the desirability of sealing a transformer against the atmosphere is now generally accepted, the influence exerted by materials of construction is not so generally understood, largely because of the complex nature of the problems involved. It is not to be assumed that because a conservator transformer gives good oil performance that the materials of construction are inert. They may only be lying inactive because of exclusion of the atmosphere, and when used in a breather-type transformer they may accelerate greatly the atmospheric effects.

The third requirement was for an oil of maximum oxygen stability. Given an oil completely proof against oxidation, the design and operation of transformers would be greatly simplified, and this is unquestionably the goal for oil development.

The practical problem at the present time, however, is the selection of an oil with the most suitable oxidation characteristics.

The first requirement (protection against oxygen access) is entirely a matter of engineering design. The two latter requirements (inert materials and oil stability) are questions which can, and should, be settled in the laboratory.

The final criterion of a transformer oil lies in its performance in service, but its long life in a transformer forces the use of accelerated tests both in making the initial choice of an oil and in ensuring the maintenance of quality in everyday supply. It is impossible also to wait for service data to show which materials are inert in oil; indeed it is usually impossible to decide which materials in a given transformer have been involved in oil deterioration, for so many factors are involved. The question of suitability of materials for use must therefore also be decided in the laboratory. As with all accelerated tests, constant arguments arise concerning correlation with service performance, but it is obvious that accelerated tests are essential.

Parts II and III of this paper will describe laboratory experiments relating to the influence of the materials of transformer construction on oil deterioration (Part II) and to the assessment of the oxidation stability of an oil (Part III).

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STUDIES IN SHALE OIL

PART III. SOME CONSTITUENTS OF SHALE NAPHTHA

By Geo. E. Mapstone (Fellow),* J. S. Durham,† and H. D. Taskis †

Summary

Among the minor constituents of Glen Davis shale naphtha, C_3 and C_4 hydrocarbons, benzene, naphthalene, and carbon disulphide have been isolated. Qualitative proof of the presence of several other hydrocarbons and classes of compounds has been obtained.

Introduction

The complexity of the classes of compounds which constitute shale naphtha is recognized. The isolation of a few constituents has been accomplished in some instances, but in the case of Australian shale naphthas, even qualitative evidence has been lacking. This paper presents such information as has been gathered concerning some of the minor constituents of Glen Davis shale naphtha, but no attempt has been made to include the major classes of constituents such as paraffins, olefins, naphthenes, and aromatics generally, as their presence and proportions have been reported previously.[1] It is considered that the results, which are summarized in Table VII, are of value in interpreting many of the properties of the naphtha, and its reactions while undergoing treatment.

Hydrocarbons

Light Hydrocarbons

Light hydrocarbons may be condensed from the retorts gases after the removal of carbon dioxide, and fractionation in a Podbielniak semi-automatic semi-robot low-temperature distillation apparatus established the presence of propane, propene, *iso*- and/or 1-butene, and *n*-butane.

Benzene

In determining the quantity of naphtha in retort gas, benzene crystals formed in the neck of the apparatus.[2] After changing from centre to side offtakes on the retorts,[3] this occurrence has been observed very infrequently and probably indicates that much less secondary cracking of the oil has been taking place.

cyclo*Pentadiene*

Afanas'ev's test [4] for *cyclo*pentadiene gave positive results with shale naphtha, while the fulvene method of Powell *et al*,[5] and the nitro prusside test of Scagliarini and Lucci [6] supported the view that *cyclo*pentadiene may be expected in shale naphtha. In addition, maleic anhydride reacted with

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some evolution of heat,[7] yielding in one case an adduct with m.p. 179° to 186° C (*cyclo*pentadiene maleic acid adduct, m.p. 177° to 179° C [8]). Tables I and II summarize the results obtained.

TABLE I

Afanas'ev Test for cyclo*Pentadiene in Naphtha*

Volume of naphtha sample *	1 drop	1 ml	5 ml
Sensitivity limit †	0·3%	140 p.p.m.	30 p.p.m.
Fresh naphtha ‡	Tint	Faint	Rich
Stock naphtha ‡	Nil	Faint	Rich

* Naphtha mixed with 1·0 ml chloroform and 1·0 ml glacial acetic acid followed by the addition of 2 to 3 drops of concentrated sulphuric acid. The formation of a violet colour was taken as a positive test.

† Assuming 0·1 mg *cyclo*pentadiene gives a colour.[4]

‡ Relative intensity of violet colour produced.

TABLE II

cyclo*Pentadiene Tests on Naphtha Fractions*

Fraction	Overhead to 60° C		160°–180° C (di-*cyclo*pentadiene cut)
	Tops to 75° C	Bottoms 75° C+	
Test :			
Afanas'ev [4]	Green (not violet)	Pale green (not violet)	Strongly positive
Fulvene with acetone [5]	Positive	Positive	—
Fulvene with benzaldehyde [5]	Positive	Positive	—
Nitroprusside in alkaline methanol [6]	Positive	Positive	Positive
Silver nitrate [9]	—	—	Reduced

Tests originally thought to indicate aldehydes (or compounds of aldehydes with ammonia) could be caused by *cyclo*pentadiene. Thus the colour formed by the action of Schiff's reagent upon naphtha (Table III) could be due to regeneration of fuchsin. *cyclo*Pentadiene is known to react with sulphurous acid. The fact that a fresh sample of Schiff's reagent (containing excess sulphur dioxide) produced no colour supports this view. Again, certain fractions of naphtha reduced neutral silver nitrate, forming a mirror. Aldehydes will not do this if ammonia is absent, but according to Lunge [9] *cyclo*pentadiene does so readily. That both of the tests cited are connected is evident from the non-appearance of a silver mirror in the case of a sample which had been washed many times with Schiff's reagent until it gave no colour.

The distribution of the fractions showing these tests is specially significant. Thus the lowest-boiling fraction (to 40° C) gave Schiff's test faintly, but no other fraction did so until 163° C (near the boiling point of the dimer). Above 163° C all fractions gave both tests in varying intensities. If it is assumed that the dimer and its homologues decompose at their boiling point into *cyclo*pentadiene and its homologues, the occurrence of the tests is explained.

TABLE III

Examination of Naphtha Fractions

Boiling range, °C	Schiff's reagent *	Neutral $AgNO_3$	Guareschi's test for phenols [17] †	$(NH_4)_2Ce(NO_3)_6$ [18] ‡
160–180	+	Faint deposit	Positive	Positive
180–190	+	Mirror	Positive	Strongly
190–195	+	Mirror	Positive	Strongly
195–200	+	Mirror	Positive	Strongly
200–205	+	Mirror	Positive	Strongly
205–210	+	Mirror	Positive	Positive
210–215	+	Mirror	Slightly positive	Slightly positive
215–220	+	Mirror	Very slightly positive	Slightly positive
220–225	+	Mirror	Very slightly positive	Slightly positive
225–230	+	Mirror	Positive	Slightly positive
230–238	+	Mirror	Positive	Slightly positive

* Old reagent. A freshly prepared reagent failed to give any test.

† Reaction with chloroform and potassium hydroxide. Positive result indicated by purplish red colour.

‡ A positive result was indicated by the yellow reagent colour changing to an orange red.

Dicyclopentadiene

*cyclo*Pentadiene polymerizes very readily to give di*cyclo*pentadiene and higher polymers on standing. A further sample of naphtha was topped to 145° C and the *cyclo*pentadiene content of the bottoms determined by the formic acid esterification procedure of Bergmann and Japhe [10] to be 0·24 per cent. This was equivalent to 0·03 per cent by weight of the original naphtha.

The maximum reduction of neutral silver nitrate (Table III) was obtained with the 210° to 215° C fraction, which would correspond to the presence of the dimer of methyl*cyclo*pentadiene.[11]

Indene

Using a naphtha fraction in the range 170° to 185° C a bright red coloration was obtained on treating with ethyl oxalate in the presence of sodium ethoxide. This would indicate small amounts of indene being present.[12-14]

It is possible that the high oxygen content of the retort gases is responsible for the relatively small indene content of the naphtha, as Brown [15, 16] found that the introduction of oxygen into hot coal gas affected the removal of indene.

Naphthalene

Although the presence of naphthalene was to be expected, as the absorption oil used for recovering the naphtha contained naphthalene, the amounts present were relatively large and variable. It was possible to isolate naphthalene by close fractionation of the naphtha, precipitation as the picrate, or by freezing. The heavier retorts light oil also contained naphthalene, which was isolated from a wide fraction by freezing, but several samples taken at different times gave negative results. A summary of these tests appears in Table IV.

TABLE IV

Naphthalene from Naphtha Fractions

Sample	Fraction, 170°–195° C	Bottoms from distillation to 180° C	Crude shale oil fraction, 195°–220° C
Sp. gr. at 60° F	0·803	0·840	—
Distillation (I.P. 123):			
10%	174° C	181° C	—
50%	180° C	193° C	—
90%	189° C	218° C	—
F.B.P.	197° C	235° C	—
Naphthalene recovered, g	3·478	n.d.	0·5
Naphthalene as % of original sample	0·295	n.d.	approx 0·1 *
M.p. of naphthalene recovered, ° C	80	79·6	79
M.p. of picrate, ° C	145·5	150·5	148
M.p. of mixed picrate, ° C	147	150	147

* Approximately 0·01% of total oil.

Inasmuch as the recovery of the crude shale oil is a low-temperature carbonization process, the occasional presence of naphthalene is suspected to be due to local high temperatures in the retorts.

OXYGEN COMPOUNDS

Phenols

Various tests for the detection of phenols in the naphtha [17] indicated their presence at an average concentration of about 0·05 per cent. The naphtha fractions (Table III) gave purple colours with Guareschi's test,[17] and the main concentration of phenols boiled between 180° and 205° C, *i.e.*, the cresol range. The presence of hydroxyl groups, probably the phenols, was indicated by the coloration obtained with ammonium ceric nitrate.[18]

Aldehydes and Ketones

All tests for aldehydes and ketones were negative, with the exception of those discussed under *cyclo*pentadiene and considered to be due to that material.

SULPHUR COMPOUNDS

Mercaptans

Mercaptans were found in all samples of fresh naphtha, as shown by a sour doctor test. The mercaptan sulphur content of the naphtha averaged about 0·025 per cent by weight, but fluctuated over the range of 0·004 to 0·04 per cent. The distribution of mercaptan sulphur with boiling range has been shown elsewhere.[1]

Disulphides

The occurrence of significant quantities of mercaptans in the naphtha, coupled with the fact that it is exposed to oxygen at high temperatures prior to recovery from the retort gas, favours the formation of disulphides. Their presence was established by reduction of the disulphides to mer-

captans by zinc dust and glacial acetic acid after removal of mercaptans with aqueous silver nitrate. The determination of the mercaptan content by reduction of the disulphides also enabled a quantitative estimate of the

TABLE V

Disulphides in Shale Naphtha

Sample	Sp. gr. at 60° F	Mercaptan sulphur, % by wt	After treatment	
			Sp. gr. at 60° F	Disulphide sulphur, % by wt
Fresh	0·759	0·0189	0·761	0·0011
Storage tank A	0·756	0·0187	0·757	0·0071
Storage tank B	0·755	0·0150	0·755	0·0012

disulphide sulphur. Results are tabulated in Table V. Polysulphides could not be detected with alcoholic silver nitrate reagent.[19]

Carbon Disulphide

Carbon disulphide was first shown to occur in shale naphtha by isolation of the zinc and copper dithiocarbamates.[1] Using IP 108/47(T), the amount of the constituent was found to range between 0·03 and 0·18 per cent by weight as sulphur in fresh samples of naphtha, the concentration being affected by the operating conditions of the naphtha plant. In some cases weathered samples were found to have lost all their carbon disulphide.

Thiophenes

Although Petrie [20] found that shale naphtha gave a positive indophenine test for thiophenes, orange to red instead of blue colours were obtained with Glen Davis naphtha. Treatment with concentrated sulphuric acid and re-distillation prior to testing did not influence the results of this test. Higher-molecular-weight thiophenes or pyrroles may possibly give the colour observed in these tests.

The presence of thiophenes unsubstituted in the 2 or 5 positions is indicated by the reduction in sulphur content of samples treated with aminomethyl sulphuric acid and formalin (Table VI).[21, 22] The results also show that acid treatment fails to remove these compounds completely.

Since, from a processing viewpoint only the classes of sulphur compounds and their distribution is of importance, no attempt has been made to isolate individual compounds other than carbon disulphide.

NITROGEN COMPOUNDS

Because of the very small nitrogen content of the naphtha relatively little attention has been paid to it. However, pyrroles were found to be present by means of the pine splinter test. Also basic nitrogen compounds (pyridine homologues) are present to the extent of approximately 0·016 per cent by weight as nitrogen.[23]

TABLE VI

Thiophenes in Naphtha

Sample	Treatment	Sulphur, wt %	
		Before Hempel distillation	After Hempel distillation to 375° F
(1) Crude retort naphtha	Nil	0·306	0·279
(2) do	250 ml sample refluxed strongly with 2·5 g AMSA * + 20 ml formalin	—	0·261
(3) do	250 ml sample refluxed gently with 2·5 g AMSA * + 20 ml formalin	—	0·248
(4) Acid treated naphtha (5½ lb/brl)	Nil	—	0·13
(5) do	250 ml sample refluxed with 2·5 g AMSA * + 20 ml formalin	—	0·11

* AMSA = aminomethyl sulphonic acid.

TABLE VII

Summary of Results

Individual Compounds Identified		
Propene	Benzene	Indene
Propane	*cyclo*Pentadiene	Naphthalene
iso- and/or 1-butene	Dicyclopentadiene	Carbon disulphide
n-Butane		
Classes of Compounds Identified		
Phenols (principally cresols)	Disulphides	Pyrroles
Mercaptans	Thiophenes	Pyridines
Classes of Compounds Absent		
Aldehydes	Ketones	Polysulphides

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PART IV. THE SULPHOCHLORINATION OF A SELECTED SHALE OIL FRACTION

By G. Nottes * and Geo. E. Mapstone (Fellow)

Summary

An olefin- and aromatic-free fraction of shale oil was successfully sulphochlorinated by means of the Reed reaction under the influence of the light of a tungsten-filament lamp.

Introduction

Because of the known reactivity and value of sulphonyl chlorides as chemical intermediates it was considered that the possibility of their preparation from selected shale-oil fractions should be examined. These products are produced by treating an oil (generally a paraffin concentrate from Fischer–Tropsch or flow oil) with a mixture of gaseous sulphur dioxide and chlorine under the influence of ultra-violet light. Since some nitrogenous constituents of flow oils have been found to inhibit the reaction [1] and the crude shale oil contains non-basic nitrogen compounds which are only partly extracted with concentrated sulphuric acid,[2] there was a possibility that the shale oil might not react.

It was also necessary to remove all olefins and aromatics prior to treatment, since the former would add chlorine and the latter would be chlorinated in the nucleus instead of being substituted to form the sulphonyl chloride. The work was carried out on an olefin- and aromatic-free sample of shale oil.

Experimental

Sulphochlorination

The 240° to 320° C fraction of the crude shale oil was exhaustively treated with concentrated sulphuric acid and redistilled to the original boiling range as described previously.[3]

A steady flow of chlorine and sulphur dioxide in the approximate ratio of 1 : 3 was passed through 100 g of the water-white oil in a gas wash bottle; the necessary radiation was provided by an ordinary 60-watt light globe alongside the bottle. The gas-flow rate was maintained sufficiently fast to effect good stirring. Evolution of hydrogen chloride

* National Oil Pty. Ltd.

soon indicated the progress of the reaction. After 3 hr the sp. gr. of the oil had increased from 0·080 to 0·897. The gas flow was then replaced by a slow current of dry air in order to remove dissolved hydrogen chloride.

Analysis of Product

The total chlorine content of the oil freed from traces of gases was determined by the Carius method, the saponifiable chlorine by refluxing the methanolic 0·5*N*-potassium hydrogen for 30 minutes, and the total sulphur content by digestion with concentrated nitric acid in the presence of barium nitrate. The precipitated barium sulphate was ignited to remove traces of organic impurities before it was weighed. The results are given in Table I.

TABLE I

Examination of Sulphochlorinated Shale-oil Fraction

	Oil charge	Reacted oil	Sulphonyl chloride *	$C_{15}H_{31}SO_2Cl$ †
Sp. gr. at 60° F	0·800	0·897	0·996	—
Total chlorine, % by wt	Nil	6·01	12·3	11·5
Saponifiable chlorine, % by wt	Nil	5·5	11·3	11·5
Total sulphur, % by wt	0·0	4·87	10·0	10·15
Saponification No., mg KOH/g	Nil	178	365	361
Unsaponifiable oil, % by wt	100	51·2	Nil	Nil

* Calculated.
† Theoretical figures for comparison.

DISCUSSION

The results indicate that it is possible to prepare a sulphonyl chloride from a selected fraction of crude shale oil by the Reed reaction. They also confirmed previous observations that the light from a tungsten-filament lamp could be used instead of the more expensive mercury arc lamps.[1]

Preliminary experiments with the reaction products of the shale-oil sulphonyl chlorides with caustic soda, ammonia, alcohols, phenols, amines, etc., indicated that they were very similar to those obtained from the sulphonyl chlorides from Fischer–Tropsch oils. It can therefore be expected that the shale-oil products would be suitable for commercial development should the circumstances prove favourable.

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PART V. ALDEHYDE RESINS FROM SHALE TAR BASES

By Geo. E. Mapstone (Fellow)

Summary

Shale-tar bases may be condensed with formaldehyde in acid solution to give acid-insoluble resins. Under suitable conditions a resin can be formed by the co-condensation of the bases and phenol. The condensation reaction appears to be analogous to that of phenol and formaldehyde in the presence of acid, first methylene groups of the α and γ side chains of the bases having a similar reactivity to the *ortho-* and *para*-positions of phenol.

Introduction

This work was commenced at Glen Davis several years ago to examine the reaction between the tar bases from cracked shale gasoline and formaldehyde.

The tar bases, which are essentially pyridine homologues with a small proportion of pyrroles, are present to the extent of approximately 0·3 per cent by volume in Glen Davis cracked-shale gasoline. In the subsequent acid treatment of the gasoline the bases are concentrated in the acid sludge from the acid treatment. This sludge is readily hydrolysed by water to give a black tar and an aqueous acid phase containing approximately 20 per cent by volume of crude bases.[12, 16] This hydrolysed acid contains some dissolved pyrroles, as do the bases liberated from it by neutralization with alkali. The pyrrole content decreases on long standing and on distillation, presumably by polymerization.

Apart from the possible commercial applications of any resinous product, it was thought that the condensation of the tar bases with aldehyde oxidation products may have been partly responsible for the rapid formation of gums in the untreated gasoline. It has subsequently been shown that, although the pyrroles present are active gum formers, the pyridine bases have a slight gum-inhibiting tendency.[15]

Jacobsen and Reimer [5] appear to have been the first to observe the condensation of alpha and gamma methyl pyridine and quinolines with aldehydes to yield 2-pyridyl or quinolyl ethanols, which may be dehydrated to the corresponding olefines. Apart from these types of products, there appears to be no reference in the literature to the formation of resins as the main product of the condensation except for a paper [19] and Russian patent by Schmidt and Petrov,[20] who condensed pyridine bases (boiling range 155° to 220° C) with formalin in an autoclave at 1·8 atm using hydrochloric acid or ammonia as catalysts. The resin cured more slowly than phenol-formaldehyde resins, but was reported to be comparable with them in film-forming, moulding, and laminating properties.

This paper outlines the work carried out to determine the mechanism of the reaction and the nature of the resins obtained.

Outline of Work Done

Preliminary investigation showed that the crude tar bases could be readily condensed with formalin at a pH less than 5 and preferably less

than 3, to give a brown, acid-insoluble product. Portion of the resinous product was soluble in acid and portion was insoluble, while some of the bases always remained unreacted. This, however, may have been partly due to the relatively mild condensation conditions employed. The crude hydrolysed acid from the disposal of the acid sludge, and containing 22 per cent of dissolved bases by volume, reacted readily. A sample of the crude resin thus obtained was submitted for examination, and was found to cure more slowly than did the phenol-formaldehyde resins. This result was in agreement, as far as it went, with that recorded by Schmidt.[19]

The initial condensation product of the bases with formalin was capable of yielding more resin when treated with an additional portion of the bases or phenol (Table IV). These resins with added phenol contained up to 4·6 per cent of nitrogen, indicating that a large proportion of the bases had been included in their formation (Table V).

Some phenols were condensed with formalin in the cold to give the resols, which were then further condensed in the presence of α-picoline. Although the polymerization of the resols was rapid, definite though small amounts of α-picoline were combined in the resins (Table VI).

Benzal chloride condensed with the shale-tar bases to give a black tar, from which half the bases were recovered by acid washing. The acid-insoluble tar was thermoplastic and benzene soluble, suggesting that it was a crude mixture of styryl pyridines. It showed strong acid-corrosion-inhibiting properties.

Mechanism of the Reaction

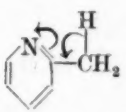
There appear to be two different possible mechanisms for the formation of a resin from the tar bases and formalin. These will be called tentatively the " phenol " and " styrene " mechanisms, and will be outlined in turn after reviewing the mechanism of the initial condensation.

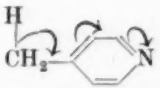
Initial Condensation

Roberts [18] has given an excellent discussion of the condensation of the reactive methyl groups of heterocyclic tertiary bases, and the mechanism he postulated is presented in a slightly modified form.

In pyridine it is well known that the following electronic displacements occur :—

In α- and γ-picolines the side chain would also be affected thus :—





indicating the incipient ionization of one of the hydrogen atoms in the methyl group and an incipient negative charge on the methyl carbon atom.

In the presence of acids the formation of the pyridinium ion greatly

increases these displacements, as shown by the greater reactivity of α-picoline methiodide than α-picoline towards aldehydes.[7]

In phenol and aniline the corresponding electronic displacements occur :—

indicating that the *ortho* and *para* carbon atoms carry an incipient negative charge.

In formaldehyde the displacement $CH_2=\overset{\curvearrowright}{O}$ will give a fractional positive charge to the carbon atom.

The essential condensation reaction of picoline, phenol, and aniline (nuclear) with formaldehyde may therefore be considered to take place as follows :—

which brings out the fundamental similarity of the reactions involved (for further details see [1]).

" Phenol " Mechanism

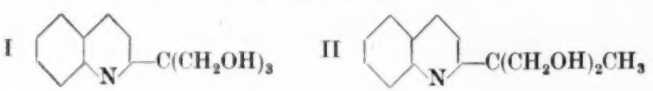
The products of the condensation of phenol, aniline, and the α- and γ-methyl pyridines with formaldehyde may be written as R–CH_2OH and the precursors as R–H. Now with phenols and aniline the secondary reaction

$$R{-}CH_2OH + H{-}R \longrightarrow R{-}CH_2{-}R + H_2O$$

takes place quite readily. Also α-picoline can yield the corresponding di-α-picolylmethane by condensation with formaldehyde.[9, 11] This supports the suggestion that the mechanism of the condensation of the reactive alkyl pyridines with formaline is analogous to the mechanism of the phenol-formaldehyde condensation, each hydrogen atom on the first carbon atom of α and γ side chains of alkyl-pyridine being reactive in the same manner as are the *ortho* and *para* hydrogens of phenols.

Because of the similarity in the reactions, phenols and α- and γ-alkyl pyridines should be capable of being condensed together if this mechanism applied, though the rates of condensation may be different.

Further evidence in favour of this theory is the formation of I from quinalidine and II from 1-ethyl quinoline.[8]



" Styrene " Mechanism

By dehydration the β-hydroxy-ethyl side chain formed by the reaction of formaldehyde with a reactive methyl side chain of a pyridine homologue

is changed to a vinyl group. Quite frequently the initial condensation product is dehydrated as formed to yield the vinyl derivative. Vinyl pyridines may be used as a partial substitute for styrene in Buna rubbers, this substitution conferring some valuable properties on the product.[2, 17, 21]

Commercial α-vinyl pyridine is inhibited to prevent polymerization during storage, a reaction which is undoubtedly analogous to the polymerization of styrene.

It is of interest to note that quaternary salts of polyvinyl pyridine and polyvinyl quinoline are mentioned in the recent patent literature.[6]

The formation of a resin by this mechanism involves the sequence of reactions :—

I. Condensation of the base with formalin.
II. Dehydration of the product to vinyl pyridine.
III. Polymerization of the vinyl pyridine.

If this is the main mechanism of the condensation of α- and γ-alkyl pyridines with formaldehyde to give a resin, then the formaldehyde-free initial condensation product of formalin and the bases would not condense with phenol, and co-condensation products of tar acids and tar bases would not be formed under these conditions.

Experimental

1. *Raw Materials*

Hydrolysed Acid. The acid sludge from the treatment of cracked shale gasoline with 5 lb of commercial sulphuric acid per brl was hydrolysed by running into a limited volume of water. The lower layer of hydrolysed acid contained 36 per cent by weight of sulphuric acid and 22 per cent by volume of dissolved tar bases.

Crude-tar Bases. Some of the hydrolysed acid was neutralized with 20 per cent caustic soda solution. The bases liberated were separated and dried over solid potassium hydroxide.

Shale-tar Bases. The purification and fractionation of a sample of tar bases isolated from the pressure distillate has been described previously.[12]

Table I

Tar Bases from Cracked Shale Gasoline

Fraction	Cut temperature, °C	Volume, %	Density at 20° C *
1	40–104	0·7	—
2	104–118	1·3	—
3	118–150	2·8	0·9347
4	150–160	1·9	0·9378
5	160–170	4·2	0·9348
6	170–180	8·3	0·9311
7	180–190	23·1	0·9305
8	190–200	28·0	0·9245
9	200–210	14·7	0·9278
10	210–212	5·8	0·9405
11	Bottoms	8·8	Tar

* Corrected from temperature of observation by data of Mapstone.[14]

The properties of the various fractions are presented in Table I. Some tests were carried out on samples of the crude bases after a straight distillation.

Treated Shale-tar Bases. The bases which had not reacted when the hydrolysed acid sludge was treated with formalin had been isolated and distilled. After standing for three years these bases are still only light yellow in colour. They were used without any preliminary treatment.

Pyridine. B.D.H. " pure " grade used without further treatment.

α-Picoline. A sample of pure α-picoline, b.p. 126° to 130° C, n_d^{23} 1·5006 was used without treatment.

Quinalidine. This was prepared by the method of Hantzsch,[4] b.p. 308° to 312° C.

Syn Collidine Dicarboxylic Ester. This was prepared by the method of Hantzsch,[4] b.p. 308° to 312° C.

2. *pH Required for Reaction*

Approximately 1 mol of crude undistilled bases (126 ml of sp. gr. 0·952, assuming average molecular weight to be that of collidine) was mixed with 1½ mols of formaldehyde (115 ml of formalin). The mixture was so dark that the pH was determined on the spot plate with B.D.H. universal indicator.

Varying amounts of conc hydrochloric acid were added to 15-ml portions of the well-shaken mixture. The pH was determined on a spot plate as before.

After standing in the cold for 48 hr, 15 ml of water were added and the effect noted. The results are given in Table II.

TABLE II

Effect of pH on Condensation

Acid, ml	pH	Aqueous phase		Oil after dilution
		Volume, %	Colour	
0	8	30	Orange	10 ml oil
1	7·75	60	Deep red	5 ml oil
2	6·5	80	Black	2 ml oil
3	6·0	100	Black	½ ml oil
4	5–5·5	100	Black	No oil—some curds
5	3–4	100	Black	No oil—heavy curdy ppt.

The sample with 5 ml of acid gave several times the amount of solid condensation product obtained with 4 ml of acid. The powder melted to a black, non-sticky tar when placed in the air-oven. After standing in the air-oven overnight the tar had solidified and swollen to a brilliant black button.

3. *Condensation of Hydrolysed Acid with Formalin*

(i) Some filtered hydrolysed acid was mixed with 4 per cent by vol of formalin and the clear red liquid stood overnight, when an appreciable amount of brown tar was deposited. The dried acid insolubles amounted to 52 g/litre of acid. The condensation product was quite soft at 70° C, but hard and brittle at 30° C. It was powdered, and the powder sintered in the air-oven. After repowdering it failed to sinter on further heating.

(ii) A similar mixture of the hydrolysed acid and formalin was refluxed for 10 minutes and the condensation product removed. It was a brittle coke and amounted to 53 g/litre of acid. A further 3 g/litre of product separated from the cold acid after standing for a week.

(iii) One litre of filtered hydrolysed acid was treated with 50 ml of formalin at room temperature. The clear solution became cloudy after ½ hr, and within 1½ hr some tar had separated. After standing for three weeks the tar cake was removed from the flask. It was black externally but light brown internally. It was dried, and then weighed 37·4 g. The acid liquor contained a heavy red brown powder which was filtered off and air dried. The total weight of dry condensation product was 56·0 g.

The filtrate was brought to the boil quickly, and boiled for 1 minute. This treatment gave a further 1·0 g of dry, very light brown powder.

The acid liquor was then made alkaline with 40 per cent caustic soda solution under reflux to prevent loss of the volatile bases. The bases were extracted with ether and the ethereal solution dried over solid sodium hydroxide.

The ethereal solution deposited a heavy tar which was filtered off, but the ethereal filtrate deposited more tar when brought in contact with concentrated sodium hydroxide solution.

The resin that had separated from the tar was boiled with conc hydrochloric acid. Part dissolved, and the rest became comparatively hard and brittle. The acid foamed strongly at first, but, as the boiling progressed, the foaming agents were apparently decomposed. The dried, insoluble resin (6·6 g) was black in colour and had the same appearance as the resin obtained by the direct boiling of the reaction mixture. The acid was neutralized with sodium hydroxide and the bases extracted.

The combined ether extracts were allowed to stand for a while, when a further 5·5 g of condensation product separated. The ether was distilled off on the hotplate, and the bases were then distilled. A further 2·5 g of condensation product was obtained as distillation residue. The distillation range of the recovered bases showed no significant difference from that of the unreacted bases.

The distribution of the condensation products is summarized in Table III.

TABLE III

Resins from Formaldehyde and Hydrolysed Acid

	G/litre
(i) Standing overnight	52
(ii) Boiling 10 minutes	53
Standing one week	3
Total	56
(iii) Standing cold for three weeks	56·0
Boiling for 1 minute	1·0
Total acid-insoluble resin	57·0
Acid-soluble resin	14·6
Total	71·6

4. *Curing Test on Tar-base–Formalin Resin*

The combined sample of resin from the treatment of the hydrolysed acid (Test 3, (iii)) was forwarded to a plastics laboratory for examination. They reported:

> "We tried out the tar base resin and we feel it worth taking further. We tried the usual moulding-powder technique, i.e. mixing with wood-flour and hexamine (to provide formaldehyde) and heating on open mixing rolls at 160° C for five minutes. The mixture sheets and is removed. It is powdered and finally cured under temperature and pressure in a mould to the shape desired. The tar base resin gave a moulded piece which was somewhat weak. We noticed that, on the mixing rolls, the mix was still plastic after the usual five minutes instead of settling hard as is usual with a normal phenol-formaldehyde moulding powder. If this indicates that the penultimate stage of the reaction is slow, then the initial condensation may have to be taken along much further. The weakness of the material may also be due to impurities in the original tar bases which may either not condense or condense in a different direction, giving useless materials which would modify the strength of the resin.
>
> "Our suggestion is that you should take redistilled rather than raw tar bases and that you should take your condensation reaction further. Enough promise is shown to warrant further work."

5. *Condensation of Pure Bases with Formalin*

The condensation was carried out as follows: A mixture of 0·5 ml base, 0·05 ml conc hydrochloric acid, 0·5 ml formalin was refluxed for 1½ hr. The condenser was then removed and the excess formaldehyde carefully boiled off. To the residue was added 0·1 ml of the base, or alternatively, phenol saturated with water, and the mixture was then gently refluxed for ½ hr.

The results of these experiments are presented in Table IV. The pyridine gave no indication of any reaction whatsoever. The α-picoline and the collidine ester did not give any resin until the initial condensation product was condensed with a further portion of the base or with phenol. Quinalidine and some of the shale-tar base fractions slowly gave some resin on refluxing with formalin, and some other fractions gave a resin on evaporation of the excess formaldehyde. In all cases, however, a resin was formed on the addition of more of the base or of phenol. In all cases the formation of resin from the initial condensation product and phenol was faster than with additional base. Also the rate of condensation with the shale-tar bases appeared to increase with the boiling range.

6. *Tar-base–Phenol Condensation*

(i) Two ml of the base were dissolved in 5 ml of conc hydrochloric acid and 5 ml of formalin, and the test-tube placed in a bath of boiling water for 1¼ hr, after which it was allowed to stand at room temperature for two months. Pure *m*-cresol (0·2 ml) was then added to each sample and shaken to dissolve. After a while the solution became cloudy and started to

TABLE IV

Condensation of Bases with Formalin

	Bases used	Initial condensation	Evaporation	+ Excess bases	+ Phenol
1	Pyridine	Nil	Nil	Nil	Nil
2	α-picoline	Nil	Nil	Soln. r. bl.	Bl. resin
3	Quinalidine	R. bl. resin	R. bl. resin	More resin	More resin
4	S. collidine di-carboxylic ester	Nil	Nil	Bl. tar	Bl. tar
5	Shale bases 118°–150° C	R. br. soln. + some resin	Same	R. bl. resin	R. bl. resin
6	Shale bases 150°–160° C	Bl. resin	Same	Bl. resin	Bl. resin
7	Shale bases 160°–170° C	L. br. soln.	Br. vis. soln.	Br. tar	Bl. resin
8	Shale bases 170°–180° C	Nil	Br. vis. soln.	Br. tar	Bl. resin
9	Shale bases 180°–190° C	L. br. soln.	D. r. resin	D. r. resin	D. r. resin
10	Shale bases 190°–200° C	Br. vis. soln.	Same	D. r. tar	D. r. tar
11	Shale bases 200°–210° C	D. r. resin	Same	D. r. resin	D. r. resin
12	Shale bases 210°–212° C	D. or. vis. soln.	R. b. vis. soln.	Bl. resin	D. r. resin
13	Treated shale bases	L. or. soln.	Or. soln.	Some or. tar	Some or. tar

Vis.	Viscous	R. br.	Reddish brown
R. bl.	Reddish black	Or.	Orange
Bl.	Black	D. or.	Dark orange
Br.	Brown	L. or.	Light orange
L. br.	Light brown	Resin	= Solid product
D. r.	Dark red	Tar	= Viscous liquid product insoluble in water

precipitate. After standing a further fortnight the resins were filtered off, washed with hot water till chloride free, and the nitrogen content (Table V) determined by the method outlined previously.[13]

(ii) A mixture of 1 ml of formalin, 2 ml conc hydrochloric acid and 0·5 ml of shale-tar-base fraction was allowed to stand at room temperature for 2 hr, after which time 5 ml of a 5 per cent solution of phenol was added. In all cases this gave immediately a whitish precipitate. On shaking, the precipitates from fractions 3 to 6 (Table I) redissolved, while those from fractions 7 to 10 did not. After standing a further 2 hr, the samples were all cloudy with some separated oil. The samples were brought to the boil rapidly, when they clarified by the formation of an oily condensation product. The solution became cloudy again, with the formation of a heavy white precipitate within 30 sec of commencing to boil. The test-tube was then stood in hot water (77° C) for 10 minutes. The appearance of the condensation product was then noted. In all cases it was a very viscous oil. After standing overnight the samples were boiled to coagulate droplets of the oily resin on the sides of the test-tube. This also produced a further white precipitate in the solution. On cooling, the buttons of resin were washed with water and the nitrogen content determined (Table V).

(iii) A mixture of 0·5 ml of tar bases, 2 ml of conc hydrochloric acid, and

TABLE V

Tar-base–Phenol Resins

Tar-base fraction, ° C	Method 1		Method 2		Method 3		
	Time to precipitate, min	N in resin, %	Colour of resin	N in resin, %	Time to precipitate, min	Colour of resin	N in resin, %
3. 118–150	5	1·96	Dark grey brown	2·47	3	Pale yellow	2·41
4. 150–160	30	—	Grey brown	1·82	50 +	Brown	2·70
5. 160–170	35	0·55	Grey brown	2·71	50 +	Yellow brown	1·36
6. 170–180	40	0·75	Orange	2·59	50 +	Yellow brown	2·96
7. 180–190	30	3·39	Orange	1·78	50 +	Grey brown	3·14
8. 190–200	50	3·79	Orange	—	50 +	Dark brown + grey tint	3·16
9. 200–210	50	4·62	Orange	—	40	Orange brown	3·13
10. 210–212	50	4·40	Orange	3·30	1	Brown	3·15

2 ml of formalin was boiled for ½ minute and then placed in a bath of boiling water for ¾ hr. The samples were removed from the bath and allowed to cool before adding to each 0·2 ml of phenol saturated with water. A precipitate formed after different times in each sample. The samples were heated in a water-bath for a further ½ hour; in each case this produced a fine white precipitate which was coagulated by bringing the solution to the boil after standing at room temperature for 2 hr. The second greyish white resin did not mix with the first darker resin, and appeared to be a phenol–formaldehyde resin. The whole sample of resin was removed, washed with boiling water, and its nitrogen content determined (Table V).

7. *Phenol–α-Picoline Co-condensation*

In this case phenol resols were condensed with α-picoline. The intermediate resols, which were not isolated, were prepared as follows:—

Phenol: 10 ml of phenol saturated with water, 25 ml of 3*N*-sodium hydroxide solution, and 25 ml of formalin were mixed and allowed to stand at room temperature for thirteen days. This gave a red, somewhat syrupy solution with a faint odour of formaldehyde. Four ml of this solution were used for the condensation.

o-*Cresol:* 10 ml of pure redistilled *o*-cresol, 40 ml of 3*N*-sodium hydroxide solution, and 23 ml of formalin were mixed and the resultant greenish solution allowed to stand at room temperature. The greenish colour had disappeared by the end of 4 hr and, on the fifth day, a white granular solid had separated from a deep wine-red solution. The white solid continued to increase in amount on further standing for a total of thirteen days. Five ml of the supernatant solution were used for the condensation.

p-*Chlor*-m-*cresol*[4] 13 g of recrystallized *p*-chlor-*m*-cresol were dissolved in 40 ml of sodium hydroxide solution. Approximately 100 ml of hot water were added to dissolve the sodium salt, which crystallized out. After the addition of 23 ml of formalin the cold yellow solution was allowed to stand at room temperature for thirteen days. Ten ml of the resultant deep-red solution were used for the condensation.

In carrying out the condensation a portion of the phenol resol solution was diluted with 40 ml of water and evaporated to approximately 5 ml to remove excess formaldehyde. The phenol and *p*-chlor-*m*-cresol resol solutions remained clear, abut the *o*-cresol resol solution precipitated a white powder

when evaporated to about 30 ml. This precipitate, which was not removed, was probably a resinous condensation product of the resol with a further proportion of the *o*-cresol. The evaporated solution was then diluted with 20 ml of water and 1 ml of picoline added. It was then heated just to boiling and acidified with an excess of 5*N*-hydrochloric acid. This gave a white precipitate which coagulated somewhat on further boiling. The *o*-cresol precipitate gave a resin on boiling, but the other two precipitates remained as curds. A portion of the phenol resol solution, when acidified and boiled without the addition of the α-picoline, gave a resin similar in appearance to that obtained from the *o*-cresol. The resins were filtered off, washed with hot water, and dried in an air-oven at 80° C for 24 hr and the nitrogen content determined as before (Table VI).

TABLE VI

Condensation of α-Picoline with Phenol Resols

	Phenol alone	Phenol	*o*-cresol	*p*-chlor-*m*-cresol
Pptd resin . .	White curds	White curds	White curds	Yellow curds
Boiled resin . .	Yellow resin	White curds	Yellow curds	Yellow curds
Dried resin . .	Dark yellow resin	Yellow powder	Dark yellow resin	Brown resin
Nitrogen content of resin, per cent .	—	0·01	0·18	0·17
Mols of picoline per mol of phenol. .	—	0·0001	0·0018	0·0021

8. *Miscellaneous Observations*

In general, the use of too great an excess of acid appeared to inhibit the formation of a resin under conditions similar to those described in the first section of the experimental work, and was probably due to the solubility of the lower-molecular-weight condensation products in acid. This was shown, in the cases where only a little acid was used as a catalyst, by the solubility of the resin in hydrochloric acid. This naturally varied with the base used, the acid strength and temperature, and the degree of polymerization. Lightly polymerized resins could be dissolved by shaking with cold dilute acid, but the more highly polymerized resins were only slowly soluble or even insoluble in boiling concentrated hydrochloric acid.

Evidence was obtained which indicated that the carbinol could be decomposed to give the original base and formaldehyde. For example, the solid white product obtained by condensing formalin and quinalidine in the presence of hydrochloric acid and precipitating with an excess of sodium hydroxide solution, gradually changed in standing, and, at the end of the seven months, had been completely reconverted to quinalidine. cf. 10, 11

Qualitative observations suggested that the crude bases and the hydrolysed acid reacted more readily to give a resin with formalin than did the redistilled shale-tar bases or the pure bases. This was not pursued further, but may have been due to the small amount of pyrroles which were present in both the crude bases and the hydrolysed acid. Caesar and Sachanen [1] found that thiophene reacted with formaldehyde in the presence of acid to

give resins in a manner analogous to the phenol–formaldehyde condensation. Pyrroles have a similar structure to thiophenes, and could therefore be expected to react similarly.

9. *Condensation of Bases with Benzal Chloride*

There was no reaction between the tar bases and benzal chloride in the cold or in the boiling water-bath even when some ferric chloride was added as a condensation catalyst.

After a mixture of equal volumes of benzal chloride and distilled tar bases had refluxed for 10 minutes hydrogen chloride fumes began to be evolved. The colour darkened and the mixture became more and more viscous on continued boiling. On cooling after boiling for 50 minutes the mixture set to a black, easily melted solid. Excess benzal chloride was present. This tar was boiled with dilute hydrochloric acid and then washed with water. Approximately 50 per cent of the original tar bases were recovered from the acid washings. The acid-insoluble tar melted on the water-bath, and did not set on prolonged heating at that temperature. It was readily soluble in benzene to give a black solution which presumably contained styryl pyridines.

10. *Acid Corrosion Inhibition by Benzal Chloride Condensation Product (Styryl Pyridines)*

(i) Some steel wool (grade 0) was damped with the benzene solution of the condensation product and then washed with gasoline. Concentrated hydrochloric acid then had no action in the steel wool even after standing in the cold (35° C) for 2 hr. A medium reaction occurred on boiling, but ceased on cooling. Concentrated hydrochloric acid dissolved approximately 2 g of untreated steel wool in 3 to 4 minutes; the reaction being so vigorous that it boiled out of the test-tube.

(ii) Five drops of the benzene solution of the condensation product were shaken with 10 ml conc hydrochloric acid, 10 ml water added, and the excess inhibitor removed by filtration. Two g of steel wool were immersed in the acid for 2 hr with the evolution of only an occasional hydrogen bubble (33° to 38° C). Hydrogen was evolved at a medium rate on boiling; about 1 g of iron dissolving in 5 minutes. The reaction rate decreased almost to zero on cooling.

Conclusions

The results presented in Table IV show that the formation of the resin took place in at least two steps—the condensation of the bases with formaldehyde followed by the condensation of the product with a further amount of the bases or alternatively, with phenol. The failure of pyridine to react while α-picoline, quinalidine, and purified tar-base fractions reacted to produce resinous products confirmed the initial assumption that the first stage of the reaction involved the active side chains of the bases. In all cases (except with pyridine) a resin was formed on the addition of more of the base or of phenol to the formaldehyde-free initial condensation product. Unless, as is unlikely, the addition catalysed the dehydration of the initial carbinol complex and the polymerization of the olefin, this reaction confirms

the " phenol " mechanism as being that principally responsible for the formation of the resins. This is further supported by the inclusion of a small amount of α-picoline in the resin from the phenol resols (Table VI), the small amount actually included being readily attributable to the high degree of polymerization of the resol prior to the addition of the α-picoline, and to the relatively slow reaction of the resol with the picoline.

The acid-soluble, alkali-insoluble product from the treatment of the hydrolysed acid with formalin was partly polymerized on drying over solid sodium hydroxide. This can be explained by the dehydration of the carbinol product, either to the olefin, which subsequently polymerized, or by condensation with a further molecule of an alkyl pyridine.

In summarizing the results it appears that the formation of a resin by the " phenol " mechanism does take place, but the " styrene " mechanism is not excluded and, under some conditions, may be responsible for a significant proportion of the product.

Caesar and Sachanen [1] co-condensed thiophene and phenol with formaldehyde to obtain commercially practicable resins. One method they found to be suitable for large-scale production was to condense the thiophene with the formalin, add the phenol, and complete the condensation. By using this procedure it is likely that the high-boiling shale-tar bases could be used commercially in the production of phenol–formaldehyde resins. However, such developments are outside the scope of this work.

Acknowledgments

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PART VI. A NOTE ON THE DISCOLORATION OF CRACKED SHALE GASOLINE

By Geo. E. Mapstone (Fellow)

On standing exposed to the air the stabilized gasoline from the thermal cracking of crude shale oil rapidly turns a brownish red. This discoloration has always been attributed to oxidation, but no clue to what reactions were involved had been previously available, although it was felt that the traces of pyrroles present may have been involved. The results reported in this note were obtained recently, partly in connexion with some other work and, since they cannot be extended, they are reported here as a possible lead for other workers.

Indoles condense with quinones to give strongly coloured condensation products,[1] and it has been found possible to make this reaction the basis of a test for indoles.[2] In deriving the test it was found that *p*-quinone developed a brownish purple to purple colour with indole (sensitivity 0·004 per cent indole); pyrrole gave similar colours, but the test was less sensitive. In each case the addition of an acid was necessary for the development of the colour. Pyridine and its homologues slowly developed a red colour with quinone in neutral solution, which became paler or even yellow on acidification.

An oxidized brownish red sample of the raw gasoline generally bleached slightly on shaking with acid (cf pyridine–quinone colour) and then slowly darkened, in agreement with the observation with pyrrole and indole. If a trace of quinone or indole (1 mg ml) was added to the pressure distillate the colour darkened very much more rapidly. These results suggest that the original red colour was due, at least partly to the formation of some quinones by oxidation, and the association of these quinones with the pyridine homologues (tar bases) which are present to the extent of approximately 0·3 per cent. On acidification, or possibly much more slowly in neutral solution, the quinones condense with the pyrroles present to give the more strongly coloured condensation product. Addition of excess quinone gave a stronger coloration, as would be expected if the pyrroles were present in excess. The more intense colour given by the addition of indole is explained by the greater sensitivity of the quinone test for indole than for pyrroles.

The reactions recorded here suggest at least a partial explanation for the discoloration of the raw gasoline on oxidation, and the possible formation of quinones as one of the oxidation products.

Acknowledgment

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Oilfield Exploration and Exploitation

Geology

636. The zone, base of biostratigraphy. K. Fiege. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (12), 2582–96.—A review of the historical development of the term "zone." Faunas cannot be used for chronological paralleling, excepting within small areas. Some rules of phylogenetic evolution are given, offering the basis for the geological measuring of time. Zone is the duration of life-time of a species which is determined phylogenetically, and whose ancestor and descendant are known. Zone, therefore, is a chronological term. The terms partial zone, subzone, horizon, and combined-continued zone sequence are explained. Discrepancies of zone sequences can be caused by wrong determination of zone fossils, careless collecting, overlooked resedimentation of fossils, different interpretation of species, migrations, and confusion of the terms zone, partial zone, and horizon. E. N. T.

637. Waltersburg sandstone oil pools of lower Wabash area, Illinois and Indiana. D. H. Swann. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (12), 2561–81.—At least 70 million brl of oil recoverable by normal primary methods has been discovered in the Waltersburg sandstone (Upper Mississipian, Chester series) of the U.S. Eastern Interior basin up to Jan. 1950. Over half is from pools in an area of about 550 sq. miles along the lower reaches of the Wabash River, and most of the rest comes from pools within 18 miles northeast, east, and southeast.

Oil in the Waltersburg sandstone of the upper part of the Upper Mississipian Chester series in the Eastern Interior basin occurs in diverse structural situations, not only on and near the crests of anticlines and the upthrown sides of faults, but also on unfaulted regional monoclines, low on the flanks of anticlines, and on the down-thrown sides of faults. Waltersburg oil is trapped in a remarkable series of bar-like sandstone bodies, some entirely surrounded by shale. Though several processes may have joined in forming these bar-like features, petrographic and stratigraphic studies point to the deposition of their well-sorted sands in a near-shore or shore-line environment by wave and current action.

Two recent major Waltersburg discoveries have resulted from facies and analysis through the projection of imperfectly known sandstone lenses into structural situations in which the lenses could act as oil traps. E. N. T.

638. Arizona wildcat checks new area. P. C. Ingalls. *Oil Gas J.*, 7.1.52, **50** (35), 117.—Northern Arizona, long recognized as a possible future oil and gas province, has been relatively untested in the past. Sinclair Oil and Gas Co. are sinking a wildcat in so far untried country west of the Black Mesa Basin and south of the Grand Canyon. The site, on the gentle southwest flank of the Kaibal uplift, is on a structure discovered by surface mapping, with Permian rocks at the surface. It is expected to drill to the

Pre-Cambrian at a depth of about 4000 ft. Most of the Palæozoic section found in the Black Mesa Basin is present here. J. C. M. T.

639. San Miguelito oilfield, Ventura County, California. H. W. McClellan and R. B. Haines. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (12), 2542–601.—The San Miguelito oilfield is on a continuation of the Ventura anticline midway between Rincon and Ventura Avenue oilfields, or 4 miles in an airline northwest of Ventura, California. The topography is rugged, with elevations reaching 1100 ft only a short distance from the seashore. The outcropping Pico (upper Pliocene) strata are deeply eroded; deep V-shaped canyons are common, and slump and slides occur in many places.

This oilfield was discovered in Nov. 1931, by means of surface geology. Accumulation occurs throughout a 2500-ft series of Pliocene sands in a closed anticline, which is on the westward continuation of the Ventura Avenue fold. The field is bounded on the north by the south-dipping Padre thrust fault, which strikes nearly parallel with the axis of the fold and on which the apparent upward displacement of the south blocks is 4000± ft.

To date eighty wells have been drilled, and development is continuing. No wells have been abandoned. Total cumulative production to June 30, 1950, was 21,595,000 brl of oil. E. N. T.

640. Age of Arkansas novaculite. W. H. Hass. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (12), 2526–41.—The purpose of this paper is to present evidence, based on conodonts, that bears on the age of the Arkansas novaculite. This formation crops out at many places in the Ouachita Mountains of Arkansas and Oklahoma, but it is well exposed at only a few localities. The best exposure known to the author is at Caddo Gap in Montgomery County, Arkansas, and most of the conclusions presented in this paper are based on a study of the conodonts collected at that place. At Caddo Gap the lower, middle, and upper divisions of the Arkansas novaculite, as well as the basal beds of the overlying Stanley shale, are exposed in cuts along the tracks of the Missouri Pacific Railroad and State Highway 8. E. N. T.

641. Jabal Ali venture. D. M. Duff. *Oil Gas J.*, 27.12.51, **50** (34), 44.—A wildcat at Jabal in the Sheikdom of Dubai, 300 miles east of Qatar has now reached 8000 ft. The section so far has included 3000 ft of salt. The well, sited on a seismic structure, follows the suspension of the Ras Sadre test well in Abu Dhabi, which, at 13,001 ft, was the second deepest well in the Persian Gulf. J. C. M. T.

642. New oil sources. Anon. *Oil Gas J.*, 7.1.52, **50** (35), 56.—In the Middle East, where present production depends entirely on structural traps, it is considered that systematic search for stratigraphic traps may well reveal a new set of equally important reserves.

Exploration in France is developing rapidly. Forty rigs are now in operation. A beginning has been made in the sedimentary basins of the Alsace valley, the Saone valley, Jura, Savoie, Provence, the Paris basin, the lower Rhine valley, and the northern part of the Aquataine basin. The 1949 Soultz-sous-Forêt discovery has proved disappointing.

In Australia there are hopes of finding commercial oil pools in the three basins of Western Australia, especially the northwest basin, which has over 17,000 ft of sedimentary rocks ranging from the Devonian to the Tertiary.

All the more promising structures in Japan have already been drilled, but conditions in the Cretaceous of the Hokkaido geosyncline are at present unknown.

One of the most important new fields in Mexico is Jose Colombo in Tabasco with a probable areas of 9000 acres, and sands aggregating 650 ft in thickness. The structure, a symmetric anticline, was discovered by reflection survey. Discovery well, completed in a 66-ft sand of Lower Miocene age at 5200 ft, had a potential production rate of 1170 b.d. of oil and 1,065,350 cu. ft/day of gas, using a ½-inch choke. J. C. M. T.

643. Australian oil possibilities. F. Reeves. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (12), 2479.—This paper is based on a number of years of field work in Australia, combined with a review of published and unpublished geological literature. A number of State and Commonwealth geologists co-operated in the field investigations.

The author points out that exploratory wells have been drilled in eight of Australia's fourteen sedimentary basins, and in only two of these basins have good showings of oil and gas been encountered. Active drilling in these two basins in late years has been disappointing. This failure to find oil in an area as large as the U.S. cannot be attributed to a lack of enterprise or technical ability, for several large foreign companies during the past ten years have spent large sums in the unsuccessful search for oil in Australia. It evidently is due to the absence of certain geological factors necessary to the accumulation of oil. The most obvious deficiency is the scarcity of sedimentary basins with a fair thickness of unmetamorphosed marine sedimentary rocks. Two or three basins on the west coast which are exceptions to this generalization may yield some oil when they are adequately tested.

There are a number of maps and some important sections. E. N. T.

Drilling

644. Penetration rates for directional drilling operations. G. Jackson. *Petrol. Tech.*, June 1951, **3** (6), 14–17.—In 1949 direction drilling service companies in the U.S.A. executed about 725,750 ft of directional hole; in the first half of 1950 the amount was in excess of 1,000,000 ft/year. The data from 405 directional wells aggregating 991,485 ft have been analysed. 267 were from California. In southern Louisiana the average rate of penetration (actual drilling time only used) increased from 105 ft/day in 1944 to 222 ft/day in 1950.

In the same area the data suggest an improvement in penetration rates at all depths. Comparisons with straight-hole drilling rates are difficult; averages based on total times showed straight holes to be about 10% faster than for oblique holes at 10,000 ft.

In California in the first half of 1950 non-drilling time was 12% of the total; in the Gulf Coast it was 16%.

In order to keep down drilling time records must be carefully studied to select the proper places to start and stop deflection work. Sometimes drift angles of 20° to 40° may be more economical than 5° to 10°. G. D. H.

645. The rheology of suspensions. Application to drilling muds. R. Mêtrot. *Rev. Inst. franç. Pétrole*, Aug. 1591, **6** (8), 294–304.—In this final part of a series on the principles of rheology and their application to drilling muds, the practical problems of the movement of mud in boreholes, such as mud loss into permeable, fissured, and cavernous formations, are discussed in relation to theoretical principles of the movement of viscous liquids in a permeable medium. C. A. F.

646. Plastic flow properties of drilling fluids—measurement and application. J. C. Melrose and W. B. Lilienthal. *Petrol. Tech.*, June 1951, **3** (6), *AIMME Tech. Paper No.* 3061, 159–64.—A commercial viscometer (Fenn V–G Meter) was modified for multispeed operation in the range 200 to 600 r.p.m. A spread of about 1100 r.p.m. could be used to get breakdown before making observations at successively lower speeds. The instrument proved sufficiently rugged for laboratory and field use. When equilibrium torque readings were obtained water-base muds with few exceptions obeyed the law of plastic flow. It was found possible to correlate the Stormer 600-r.p.m. visc with the plastic visc and yield value, and the initial gel readings for the two instruments.

The effects of chemical treatment on yield value and viscosity were studied.

The pressure drop of a mud in laminar flow, *e.g.*, in a well annulus, will depend on the plastic-flow properties. In order to make pressure-drop calculations, knowledge of the effect of temp on the plastic-flow properties is required, because the yield value at average well temp may be considerably greater than that measured at the surface. G. D. H.

647. A modified low-strength cement. B. E. Morgan and G. K. Dumbauld. *Petrol. Tech.*, June 1951, **3** (6), *AIMME Tech. Paper No.* 3062, 165–70.—High-strength cements present difficulties because there may not be satisfactory penetration with gun-perforation, while severe cracking and shattering may contribute to failure to exclude gas or water. It has been shown that these troubles may be reduced by using 150 p.s.i. tensile strength rather than 300 p.s.i. It is not easy to make the perforations

at the time when the strength has the lower value, and so a low-strength cement may have advantages. High early strength cement and normal Portland cement have been modified by adding 12 to 15 lb bentonite and 0·5 lb calcium lignosulphate per sack with 10 and 9 gal, respectively, of water. The pumpability of the modified cement slurries was similar to that of conventional slow-setting cement, but the permeability was higher, although still deemed satisfactory. The seven-day tensile strength was 200 p.s.i.; conventional cements gave values of 398 to 667 p.s.i.

In surface tests the modified cement had greater penetration than conventional cement by bullet or jet, and little or no fracturing. The modified cement slurry remains in suspension until set; conventional slow-set cements show water separation. The modified cement slurry has lower density than the conventional slurry, and so there is less danger of loss of circulation.

The results of a number of field tests are summarized. The time and expense of stage cementing can be avoided when there is risk of lost circulation with long fill-ups. There appeared to be satisfactory perforation and absence of shattering. The modified cement has no particular advantage in squeeze cementing unless the hole section is enlarged and subsequent perforation is needed. The modified cement is cheaper than conventional cement (no allowance for cost of mixing the ingredients). G. D. H.

648. An analysis and the control of lost circulation. G. C. Howard and P. P. Scott. *Petrol. Tech.*, June 1951, **3** (6), *AIMME Tech. Paper No.* 3096, 171–82.—Loss of mud circulation may be due to natural fractures, induced fractures, cavities in limestones or unconsolidated formations. The features of each of these causes of loss are described. For effective treatment it is desirable to know the cause of the loss. It is probable that fractures are commonly induced or widened during drilling due to mud pressure arising from excessive weight, high pump pressures, or surges arising when the drill-pipe is lowered rapidly.

It is believed that the presence of effective lost-circulation-combating material in the drilling mud would serve to plug small fractures when they are encountered or created, and so reduce the risk of lost circulation by preventing widening and extending of the fissures.

A number of materials have been tested in simulated fractures and shallow wells. Granular materials were more effective plugging agents than lamellar or fibrous materials, and coarse materials were more effective than fine. In some cases pumpability fixed an upper concentration, and so the comparisons were not always on the same basis. Proper size gradation is needed in the materials used.

There are indications that dehydratable materials are effective for regaining circulation. G. D. H.

649. Quantitative application of radioactivity logs. R. E. Bush and E. S. Mardock. *Petrol. Tech.*, July 1951, **3** (7), *AIMME Tech. Paper No.* 3075, 191–8.—A device for determining the position of zero radioactivity has been introduced in logging, as well as a sensitivity selector switch. These are employed to obtain logs in order to compare neutron curve deflections with core porosities in limestone fields, and then obtain a neutron-derived porosity curve which can be applied to wells for which there are the radioactivity logs only.

The neutron-productivity number is discussed. It is a relative method using a factor derived from the γ-ray and neutron curves. Its value at a given depth aids in fixing gas/liquid contacts in shaly sands. The application is limited to areas and reservoirs where the neutron curve is definitive of gas in the reservoir. G. D. H.

650. Application and interpretation of hydrocarbon well logging. J. E. Bliss. *Oil Gas J.*, 9.8.51, **50** (14), 76.—The advantages claimed for the use of continuous hydrocarbon well-logging in exploration wells are: (i) every gas or oil-bearing section will be detected as it is drilled, no potential pay being overlooked; (ii) coring and drill-stem testing can be confined to promising horizons, and the drill-stem tests may be performed at once, minimizing risks of mudding-off.

Mud and cuttings are investigated for gas by passing air drawn through the agitated mixture over a heated filament. The presence of gas, by igniting, raises the temp of the filament, and the accompanying rise in resistance is detected by a suitable bridge circuit and recorded. It is possible, by varying the temp of the filament, to dis-

criminate between methane and other gases. One part of gas in 2500 parts of air can be detected.

To detect oil, cuttings are first subjected to U.V. light. Fluorescent cuttings are solvent-tested to distinguish oil from mineral fluorescence.

The essence of the logging method is that samples are tested at 2-ft-depth intervals (allowance being made for current rate of drilling and lag of cuttings from formation to surface), thus giving a continuous record which is plotted alongside depth, drilling rate, and a visually determined record of lithology and porosity. In interpretation, significant shows of hydrocarbons are those which accompany changes of lithology and porosity. The article is accompanied by a number of examples of logs of the above type with an interpretation of each to show the method of reasoning adopted.

J. C. M. T.

651. Advancement in design and technique of rotary fishing tools. F. L. Scott. *Petrol. Tech.*, June 1951, **3** (6), 18–19.—Load and stretch measurements made on the rig floor have made it possible to locate the approx sticking point of drill-pipe prior to making a cut. Outside cutters were developed. Some are screw-fed, others weight-fed. In 1946 the electronic strain-gauge principle was applied to locating the sticking point, and in 1947 explosive jar blows at tool joints were successfully applied in association with left-hand torque. This has led to the greatest efficiency in drill-pipe recovery yet attained.

There have been improvements in the technique for maintaining straight hole, so eliminating " dog-legs " and key-seats.

The jar safety joint is a boon, and can be applied upwards or downwards as soon as pipe sticks. Drill-collar stabilizers or key-seat wipers also aid in removing key-seats or ledges.

The hydraulic pulling tool is of great value in removing tools from cased holes. Pulls far greater than the capacity of the rig can be applied. Entire liner strings several hundred ft long have been easily withdrawn in one application. G. D. H.

652. Masts and towers for drilling and production. S. Karlic. *Nafta*, Jan. 1951, **7**, 9–11; Feb. 1951, **7**, 36–9.—Towers and masts are playing the part of fulcra in a system of levers which is designed to win oil from the ground. They must be capable of withstanding the exceptional momentary strains for which the power supply is designed. Formulæ and diagrams for design of such derricks are given. M. S.

653. Pressure and tension gauges (dynamo-meters) for petroleum industry and their applications; experimental results of tests on models of wired masts. J. Ostaszewski. *Proc. of Main Petroleum Institute*, (Polish) *Ministry of Mining*, Cracow, 1951, **No. 5**, Pp. 19.—Two papers, the first of which describes some twelve gauges, their principles; construction, use, and applications. Second paper deals with models as a medium for determining stresses and gives an example where full-scale model proved better than calculations led to expect. Diagrams and formulæ are included. M. S.

654. Researches on the radioactivity of rocks of oil wells. M. Miesowicz *et al.* (collected papers). *Proc. of Main Petroleum Institute*, (Polish) *Ministry of Mining*, Cracow, 1951, **No. 4**, Pp. 16.—Three short papers previously read before the (Polish) Petroleum Institute are presented in the form of a brochure. Their titles are " Gamma-logging apparatus with continuous recording for petroleum drill-holes," " Interpretation of electronic logging using apparatus equipped with integrating and recording device," and " Measurement of gamma and beta radiation from drilling samples."

M. S.

Production

655. The Shannon sand reservoir, Cole Creek field, Wyoming. E. J. Whitaker and D. J. Hoenshell. *Petrol. Engr*, 15.7.51, **23** (8), B-42.—The Cole Creek structure in the Powder River Basin, 20 miles northeast of Casper, Wyoming, was detected by torsion balance and seismic surveys in 1936. The first Shannon producer was completed in 1940, and produced 430 b.d. on pump; original production was from the Dakota–Lakota. Twenty-five wells are currently producing.

The Shannon structure is elliptical with low relief, and pay averages 17½ ft. The crest is at 1120 ft above sea-level. Producing area was originally 1620 acres, with water at 980 ft above sea-level. The sand is fine to medium grained, porosity averaging 19%, connate water 31%, and air permeability 56 mD.

There is a close relation between reservoir pressure and withdrawal rate. Water injection was started in 1946 and increased in 1950. Total vol injected is approx 670,000 brl. By using "bubble-point" pumps in the wells producing pressures to within 150 p.s.i. of the bubble-point pressure have been maintained.

It is estimated that ultimate recovery efficiency will be over 36% due to the injection programme. The field is unitized.

Reservoir data, performance curves, and a structure map of the Shannon are included. C. A. F.

656. New life for Abqaiq. D. M. Duff. *Oil Gas J.*, 27.12.51, **50** (34), 46.—A large-scale pressure-maintenance programme is planned for the Abqaiq reservoir in Saudi Arabia, and should be completed in 1953. Abqaiq reservoir, 32 miles by 6, ranks in size with East Texas and Burgan fields, and at present produces 550,000 b.d. About 300,000 b.d. of this is accounted for by natural water-drive, but this is insufficient to maintain pressure at a level high enough for expected future production. This water drive is supplied by an aquifer common also to the Ain Dar field and the newly discovered Uthmaniyah field, and a drop in pressure at Ain Dar has been noticed resulting from production at Abqaiq. In the plan over 150,000,000 cu. ft. of gas will daily be returned to the reservoir. Pressure gradients throughout the field are uniform. A well, now shut in, on the crest of the structure will be employed for the initial gas injection.

A water-flood programme is also under consideration. J. C. M. T.

657. The Southwest Antioch Gibson sand unit. T. E. Ockershauser. *Petrol. Tech.*, July 1951, **3** (7), *AIMME Tech. Paper No.* 3057, 199–204.—The Gibson reservoir had no original gas cap, and no water drive. The initial reservoir pressure was 2925 p.s.i., shrinkage was 70%, connate water 15%, porosity 15·5%, permeability 1— to 1000+ mD, and gas/oil ratio 1340. Primary recovery methods were predicted to give 22,000,000 brl from a 137-acre tract. Unitization and gas injection are expected to make the yield 41,000,000 brl. There are now 137 wells in the unit. The original participation formula based half of tract interest on net pay and half on ability to give up to 150 b.d. with a max of 375,000 cu. ft. of gas. Oil is taken from the wells which will produce with the least loss of reservoir energy reasonably practicable. G.O.R.'s are measured monthly, and reservoir pressures three to four times a year.

Injection of 9 M.M.c.f/day of processed gas began in Aug. 1948. A capacity of 25 M.M.c.f/day was reached in June 1949. There are seven injection wells, all in high positions near the eastern edge of the sand. Over 10,000,000,000 cu. ft. of gas has been injected in twenty-one months. The first beneficial effects were noted after two months. There were reduced rates of pressure fall, higher oil rates, lower gas/oil ratios, and higher oil gravities (API). The gas front has advanced uniformly.

137 wells had given 10·8 million brl of oil to Mar 1950, 85% having come from eighty wells in the first enlarged unit. When unitization began the G.O.R. was 2900 and rising rapidly. It is now 4800, but was expected to have been over 10,000 had there been no gas injection. Before unitization the production was 7370 brl/p.s.i. pressure drop; since that date it has been 17,790 brl/p.s.i. pressure drop. G. D. H.

658. Offshore production and completion practices. J. L. Le Blanc. *Petrol. Tech.*, July 1951, **3** (7), 13–15.—The Bay Marchand and Main Pass fields are each about 3 miles offshore in the Gulf of Mexico. Both are associated with salt domes, the former producing from thirteen super-cap sands at depths of 2350 to 5700 ft, while the latter has four producing sands at depths of 5500 to 8150 ft. Bay Marchand has much peripheral and radial faulting. Directional wells have been drilled from platforms, and angles of 18° to 25° are normally used, but as much as 54° has been reached. Three types of gravel packs have been used, the open-hole pack giving the best productivity indices, but being costly. Single-stage packs showed plugging early.

Many of the production problems have been solved by installing automatic separating and pumping equipment offshore. The horizontal separator is 20 ft long and 5 ft dia,

being constructed to withstand 125 p.s.i. It acts as separator, surge tank, test tank, and free-water knockout. A complete production unit for a platform consists of two of these horizontal low-pressure separators, two conventional horizontal high-pressure separators, a pipeline pump, well-head safety valves, and pneumatic controls.

Electrically driven pumps are used at Bay Marchand and internal-combustion-engine-operated pumps at Main Pass. Two gaugers are employed on each field instead of the six under the old system. G. D. H.

659. Steady flow of two-phase single-component fluids through porous media. F. G. Miller. *Petrol. Tech.*, July 1951, **3** (7), *AIMME Tech. Paper No.* 3079, 205–16.—The fundamental equations are set out for describing the flow and thermodynamic behaviour of two-phase, single-component, steady state fluid flow through porous media. The analysis concerns adiabatic, microscopically linear flow through a horizontal column of porous matter. The fluid enters the upstream end in the liquid state, but after moving downstream begins to vaporize and moves as a gas–liquid mixture for the rest of the path.

The weight rate of flow and pressure distribution are determined for a given inlet pressure and temp, given exit pressure or temp, and given characteristics of the test fluid and porous medium. Phase equilibrium is assumed.

The theory is supported by laboratory work using propane. The apparatus, materials, and procedure are described. Capillary pressures and their gradients are concluded to be of negligible magnitude in the system used. G. D. H.

660. Determining interstitial water saturation. H. I. Meyer. *Oil Gas J.*, 14.1.52, **50** (36), 113.—Following a brief study of the physical principles involved, a critical survey of present methods of determining the interstitial water saturation of reservoir rocks is made. Two classes of method are recognized. One makes use of direct measurement of properties of the rock *in situ* or on cores taken from the reservoir; the other examines cores by some method which attempts to reproduce in the laboratory conditions believed to apply in nature in the reservoir. A criticism of the first type is the possibility of misleading results arising as a result of the use of drilling fluids. Of the second class the restored-state or disk method, the centrifugal method, and mercury-injection method are discussed. Of the first, the evaporation method is much criticized, while the author states that the resistivity method is the most favourable weapon of all, although much further field and laboratory study is required before it can be used effectively. J. C. M. T.

661. Water floods in Greenwood County, Kansas. Anon. *Oil Gas J.*, 27.12.51, **50** (34), 60.—Many fields in Greenwood County, which include the famous Bartlesville Shoe String fields, are now operating under water flood. The article summarizes the history of development of the area as a whole, and includes details of water-flood practice in each of forty-nine separate fields or units. It is estimated that of the 178,000,000 brl produced up to July 1951, more than 20,000,000 have been recovered by water flooding. The average water-flood recovery exceeds 2000 brl/acre. Water is taken from the Douglas and Arbuckle formation; surface water is also used. Details of treatment are given in the tabulated summary. J. C. M. T.

662. Gravel pack completion for exclusion of gas and water. T. S. West. *Petrol. Tech.*, June 1951, **3** (6), *AIMME Tech. Paper* No. 3060, 183–90.—A gravel pack of alternate layers of different sizes has been built round a slotted liner. The top of the pack is sealed by quickset cement and sand, while tubing with a packer is run into the liner. The pack extends almost through the sand. If the upper part of the sand contains gas, and the packer is set below the gas–oil contact and casing, mud above the packer will enter the coarse layers of the pack, but not the gas sand or into the fine layers. If its head is greater than the formation pressure the gas will not enter the well, but fluid production is obtained below the packer through both coarse and fine layers. The optimum producing level can be found by experiment after completion. By means of a suitable double-packer assembly a shut-off can be obtained both above and below the producing zone.

An alternative shut-off is by pumping oil down between the casing and tubing, and this enters the gas sand, giving oil saturation above the zone where gas coning would

normally occur. Any tendency to gas cone causes this oil to flow down and be produced instead of gas. The same technique may be used to suppress the effects of a tendency towards water coning, provided suitable packers are employed.

Three typical field cases are discussed in detail. About 100 wells have been completed with this type of gravel pack. Six were failures, and five had cement failures. In one instance there was success with a 2-ft oil column below 33 ft of gas. Two developed high gas–oil ratios evidently due to vertical coning, but the gas was successfully controlled by continuous oil injection. In two cases a water shut-off was obtained using two packers, while the water output was halved in another case. G. D. H.

663. Experimental foundations for production of iodine and bromine from Polish deep salt waters. W. Chajec. *Proc. of Main Petroleum Institute*, (Polish) *Ministry of Mining*, Cracow, 1951, **No. 3**, Pp. 25.—Beginning with analyses of various underground salt-water reservoirs the author gives details of pilot-plant extraction of iodine and bromine and the economics of such processes. Several tables, diagrams, and graphs are included in the brochure. M. S.

664. Mechanics of crude pumping equipment. Z. Turkowski and S. Karlic. *Proc. of Main Petroleum Institute*, (Polish) *Ministry of Mines*, Katowice, 1951, **No. 9**, Pp. 43.—Brochure consists of two papers: first "Problem of the dynamics of conjugated power system" gives an analysis of forces in such a system and can be used when such system is designed. The second, "Mechanics of surface pumping arrangements for crude oil" gives a full description of all components of pumping system, reduction gears, and motors. Diagrams and formulæ for calculation of forces and power required are also given. Graphical and analytical methods are used. M. S.

Oilfield Development

665. Development of the Susan Peak field. D. W. Graham. *Petrol. Engr*, Nov. 1951, **23** (12), B-7.—The Susan Peak field, Tom Green County, Texas, was discovered in Dec. 1948 by 1-A Green. Three pays have been found at approx 4500 ft in a structural trap which lies on the eastern shelf of the Midland Basin. These are the Upper and Lower Strawn limestones and the Canyon. The Lower Strawn, which has high porosity, is the main producer.

Sixty-two producers had been completed to Sept. 1951; forty-seven in the Lower Strawn, thirteen in the Canyon, and two in the Upper Strawn.

Structure contour maps and an electric-log cross-section are included. C. A. F.

666. Exploration operations in Pakistan. Anon. *Petrol. Engr*, Nov. 1951, **23** (12), B-12.—A well is being drilled on an anticline at Sui, Dera Bugti, in Baluchistan. Approx 5000 sq. m. at the southern end of the Sulaiman range have been explored using aerial and surface mapping. C. A. F.

Transport and Storage

667. Size and speed of tankers. J. Lamb and R. L. Brown, *Motor Ship*, Oct. 1951, **32** (379), 264.—This extract from a paper read at the World Petroleum Congress (*Proc. World Petrol. Cong.*, 1951, **9**, 162–9) discusses recent improvements in the construction of tankers. During the past twenty years there has been a phenomenal growth in the world's oil-tanker fleet, but apart from the introduction of welding as a method of construction, improved living-quarters for officers and crew, and the provision of aids to navigation and labour-saving appliances, tankers building to-day are not very different from those of twenty years ago, except that they are larger and faster. Deadweights of the largest tankers have gone up from 12,000 to 30,000 tons, and speeds have increased from 12 to 16 knots. The subject is considered under the headings port facilities, speed of tankers, quantity of cargo carried by fast and slow tankers, reserve power, designing a tanker, and welded construction. U. M.

668. The "Auricula's" increased speed on boiler oil. Anon. *Motor Ship*, Dec. 1951, **32** (381), 337.—A tabulated abstract is presented of engine performance between

July and Oct. 1951. The fuel used is of 3340 sec Red. No. 1 at 100° F, and that generally supplied to the ship is within the range of 3000 to 3500 sec, as normally used by oil-fired steamers. U. M.

669. Another British tanker launched. Anon. *Petroleum*, Jan. 1952, **15** (1), 13–14.—A description of the oil tanker *Velletia* built for the Anglo-Saxon Petroleum Co. Ltd., This ship, a sister ship to the *Velutina*, is designed to carry a cargo of 26,000 tons at 50 cu. ft/ton 98% full. The designed service speed, fully loaded, is 15 knots, the dead-weight about 28,000 tons on 34 ft draught. R. E. P.

670. A 500-ton petroleum barge. Anon. *Motor Ship*, Dec. 1951, **32** (381), 345.—Description and illustrations of a barge under construction for Esso at the Hessle shipyard of Henry Scarr Ltd. The 500 tons of petroleum spirit, the max allowed by the P.L.A., are carried in seven tanks. Cargo space is separated by cofferdams forward and aft and by spaces at sides and beneath tanks, a precaution against oil leakage into the river in the event of damage to the shell. Dimensions of barge are: L.O.A. 168 ft, breadth 32·5 ft, draught 8·5 ft, deadweight 518 tons, service speed 8·5 knots. For main propulsion there is a four-cyl Crossley engine developing 400 b.h.p. at 500 r.p.m. and driving a propeller through an S.L.M. 2 : 1 reverse-reduction hydraulic gear-box. There are three 45-b.p.h. Crossley diesel engines for auxiliary purposes, two of which are clutch-coupled to the two cargo pumps in the after cofferdam. Each of these pumps has a capacity of 175 tons/hr, enabling the ship to be completely discharged in 90 min. U. M.

671. Plantations's big-inch expansion. P. Reed. *Oil Gas J.*, 6.12.51, **50** (31), 107.—The 707-mile parallel line of 18- and 14-inch project is reviewed. Estimated future capacity will be 221,000 b.d.

Advanced operating techniques are employed, twelve intermediate pumping-stations eliminated, and deliveries speeded up by segregation of fuel oil into the smaller line. G. A. C.

672. Heat insulation aspects of long petroleum pipelines. K. Seiffert. *Erdöl u. Kohle*, 1951, **4**, 698–704.—Review of factors affecting heat losses in long crude-carrying pipelines. For viscous crudes (*e.g.*, Germany, Middle East) the operating temp should be 30° C min, hence choice must be made between lagging and installation of intermediate heating equipment so as to give optimum conditions at lowest cost. Expressions for calculating heat loss in lines are considered, and various types of lagging are described, with diagrams. Description is given of planning and construction of a 16-km 125/133-mm-dia pipeline in the Emsland. First 8 km were lagged with double glass-wool matting of 80 mm thickness, the remainder with a slag-wool covering, also of 80 mm thickness. With an initial temp of 78° C and air temp of 6·5° C, a water flow thermally equivalent to 8900 kg/hr of crude was delivered through above pipeline at 30° C final temp. Test results of temp measurement at various distances along the line agree well with calculated values. P. V.

673. Transient flow in gas transmission lines. R. H. Olds and B. H. Sage. *Petrol. Tech.*, July 1951, **3** (7), *AIMME Tech. Paper No.* 3081, 217–22.—The principles of the conservation of momentum and material have been applied to long gas pipelines. The length is such that the characteristics of flow can be considered independent of the position in the cross-section. The solutions of the problems take note of variation in friction and specific volume of the fluid as functions of time and position.

In one case the time–pressure relations at the exit of a 122-mile pipe were determined when flow at the inlet was stopped, but there was withdrawal at the rate of 300×10^6 cu. ft/day at the outlet. There was little or no change at the exit for 45 min, but the limiting exit pressure was reached in 280 min.

In the other case the line consisted of 165 miles of single pipe and 49 miles of two parallel pipes of the same dia. The input rate was 300×10^6 cu. ft/hr. The withdrawal rate varied during each day, but aggregated 300×10^6 cu. ft/day. The pressure variations at different points in the line were determined.

A graphical approach employing successive approximations is described.

G. D. H.

674. Main principles for calculation of a petroleum hydraulic pipeline. S. Rachfal. *Proc. of Main Petroleum Institute*, (Polish) *Ministry of Mining*, Katowice, 1951, **No. 7** pp. 22.—A summary of formulæ for isothermal flow of viscous liquid along a pipe, and for determining friction losses.

During winter viscous fluids have to be warmed before pumping. Heat correction depends on conditions of pumping, and formulæ are given for calculating friction in non-isothermal flow. Illustrated by solved examples. M. S.

675. Pipeline scraper traps. P. Reed. *Oil Gas J.*, 27.12.51, **50** (34), 56.—Scraper-trap and piping details are discussed, including dia and length of barrels, features of launching and receiving barrels, advantages of quick-opening flanges, details of by-pass lines, and installation of vent valves and line valves.

Special situations demand traps out of the conventional, and unnecessary traps should be eliminated.

Ten figures illustrate the article, and a table of max scraper lengths is given.

G. A. C.

676. All weather microwave communications for pipelines. J. Racker. *World Petrol.*, 1951, **22** (12), 86–9.—Several pipelines up to 1500 miles long have been equipped with micro-wave communications. Advantages of this method over longer wave-lengths and wire links include virtual freedom from climatic and electrical interferences. Inital and operating costs are comparatively low, installation is rapid, with few right-of-way problems, and facilities may be rapidly expanded; as many as twenty-three simultaneous conversations may be carried over one link. Other electronic circuits may be added to give remote control of valves and transmit meter readings.

E. B.

677. Calculated and experimental determination of storage losses for light hydrocarbons. G. Daric. *Bull. Ass. franç. Tech. Pétrole*, 1951 (90), 49–85.—Fundamentals of v.p. relationships and of evaporation, breathing, and filling losses are considered, with diagrams. Ten general basic formulæ are derived covering: vol of saturated air corresponding to loss of unit vol of product; vapour concn in such air at 27° C; daily breathing loss from tank having vent pressurized at given val; pressure required to prevent any breathing loss from a tank; vol changes with temp in const-pressure tank; pressure changes with temp in const-vol tank; filling limit for empty tank so as to avoid loss through vent; loss on complete filling of tank, as a function of vent pressure; loss on partial filling of tank, as a function of vent pressure; loss occurring on simultaneous filling and emptying of inter-connected tanks. "Economic pressure" of a tank is considered, *i.e.*, the pressure leading to least annual financial loss taking operational (*i.e.*, product loss), maintenance and standing charges into account. The various examples given are also depicted graphically. Experimental determination of loss can be either by actual gauging or by measuring changes in product characteristics. Latter method (change in v.p.) is considered more convenient and accurate.

V. B.

678. Storage and transport of natural gas. Z. Wilk. *Proc. of Main Petroleum Institute*, (Polish) *Ministry of Mining*, Cracow, 1950, **No. 2**, pp. 12.—The consumers of national gas are industry and householders. Their needs vary seasonally and from hour to hour. Steady production will cope with such demands only if gas-holders are used. If gas is to be conducted over large distances compressors are necessary and loss of pressure is calculated and plotted. A formula giving the most economical pipe-line dia is given. Other problems resulting from deviation from ideal gas laws, seasonal fluctuation of consumption, liquefaction, and mixing with town gas are all dealt with. M. S.

Refinery Operations

Refineries and Auxiliary Refinery Plant

679. Third A.I.O.C. refinery in U.K. has many new features. Anon. *Oil Gas J.*, 20.12.51, **50** (33), 310.—The construction of the new Anglo-Iranian Oil Co.'s refinery at Medway, Kent, is reviewed.

A large distillation unit of 80,000 b.d. capacity, two 17,000-b.d. vacuum distillation units, and a catalytic cracker of 10,000 b.d. capacity are being installed.

Four jetties capable of accommodating craft up to 32,000 tons are being constructed. G. A. C.

680. How 10 control problems were solved at Cities Service Plant. E. D. Mattix. *Oil Gas J.*, 6.12.51, **50** (31), 88.—Subjects cited include priming facilities for unloading crude oil from barges, steam–air decoking of furnaces, compressor-suction pressure-loss, surging of sidestream level, controllers, removable thermo-welds and protective guards, dual-range mercury manometer flow meters, mixers, reducing noise in cat-cracking unit, pH control of overhead water draw-off from crude-oil units, and controlling flow of 50° Baumé caustic. G. A. C.

681. Caltex-Fiat builds 97 mile pipeline and 25,000 brl refinery in North Italy. H. B. Nichols. *Oil Gas J.*, 20.12.51, **50** (33), 232.—The new refinery being built near Milan to produce a line of basic products, including straight-run and reformed motor fuel, kerosine, automotive and heavy diesel, and residual fuel oil, is described, together with the 8-inch line to the discharge terminal at Savona. G. A. C.

682. Winnipeg refinery designed to produce complete product range. Anon. *Oil Gas J.*, 20.12.51, **50** (33), 249.—The 12,000-b.d. plant of Imperial Oil Co., Canada, which incorporates an atmospheric and vacuum distillation crude unit, plus catalytic cracking for 3400 brl of fresh gas-oil feed, and gas-concentration facilities is described.

Three flow sheets are given. G. A. C.

683. Winnipeg refinery begins operation. H. C. Plummer. *Petrol. Engr*, 1951, **23** (8), C5.—Details are given of the building of a new $10 million refinery at Winnipeg, with refining capacity of 10,800 b.d., and cat-cracking capacity of 3000 b.d. E. K. J.

684. Flexibility achieved by modernization. A. L. Foster. *Petrol. Engr*, 1951, **23** (10), C11–14.—The modernization of Tyler, Texas, refinery, from a conventional crude topping and thermal cracking plant to a plant capable of producing products of specifications required by present and future market demands is described. A new fluid cat cracker of 4000 brl charge/day capacity has been installed together with water-treatment and crude desalting units. The latter is required by the high salt content of the crude—40 lb salt/1000 brl crude. Detailed description of the old and new plant is given. E. K. J.

685. Montreal modernization doubles refining capacity. H. C. Plummer. *Petrol. Engr*, 1951, **23** (10), C24.—A detailed description is given of the expansion of Montreal East refinery, which has more than doubled its capacity to 40,000 b.d. Intermediate storage is eliminated as far as possible to cut down heat losses, and propane recovery is carried out at high pressure to reduce the size of the condenser. Scope for expansion according to market requirements has been allowed for. E. K. J.

686. Oil refinery in the Canaries. Anon. *Petroleum*, Feb. 1952, **15** (2), 37–8.—Describes the refinery, owned by the Compania Española de Petroleos (CEPSA), which is operating at Teneriffe in the Canary Islands. Originally a simple crude-distillation unit, thermal cracking was added in 1935, and now there are complete facilities for the production of high-grade lubricating oils. The latest addition to the refinery comprises a two-stage crude-distillation unit of 5000 b.d. capacity, a furfural refining unit, an MEK-benzole solvent dewaxing unit, a propane de-asphalting plant, and clay percolation for the filtering of lubricating oils to colour specifications. A de-asphalting plant has also been added for the separation of asphalt from residues to give a stock which can be processed as a lubricating-oil stock for the production of bright stock, a high-visc lubricating oil.

Two widely different types of crude are processed—viz., a 34·9° API gravity Arabian crude and an 18·1° API gravity Venezuelan crude. R. E. P.

687. Beating the alloy shortage. V. B. Guthrie. *Petrol. Process.*, 1951, **6** (12), 1361–4.—A brief general review is given of the Interdivisional Symposium on the "Outlook for steel" held during the API Ann. Mtg, Nov. 6, Chicago. Mention is made of the five chromium–molybdenum steels proposed by the API interim advisory committee as standard for refiners to use as a conservation measure. The following two papers presented at this meeting are given in full: "Some problems incident to alloy steel substitution in petroleum refineries." C. H. Samans. The value of the alloying metals chromium, molybdenum, vanadium, nickel, titanium, and columbium is discussed, and reasons given for the non-feasibility of a great reduction in their use by the petroleum industry. "Conservation of critical alloys." N. J. Rees. Examples are cited of the conservation of alloy steels in the refining industry by the use of carbon steels and alloy steels containing reduced quantities of alloy metals under conditions normally considered unsafe. This practice is considered sufficiently sound owing to the highly developed and efficient maintenance and inspection departments of refineries. D. W. F.

688. Cost estimating for refineries. R. P. Wilson. *Petrol. Engr*, 1951, **23** (10), C39–42.—The procedure is outlined for obtaining an estimate of plant construction costs from flow diagram to construction details of the plant components. Useful methods are given for approximating the cost of the whole plant and of individual items. Possible sources of inaccuracy in the final estimate are traced. The cost of the detailed estimate must first be justified in the light of current economic conditions, and then the most accurate figures must be found for the cost of each item. The final job cost should always be compared with the estimates and the inaccuracies analysed. E. K. J.

689. Chemical circulation cleaning of towers. V. E. Bowes. *Petrol. Engr*, 1951, **23** (5), C5.—Water-cooling towers can be cleaned by the continuous circulation of chemical detergents, which has the advantages of shorter cleaning time and more efficient cleansing. The choice of the most suitable detergent depends on the composition of the deposits in the towers. E. K. J.

690. Wheatstone bridge in cooling tower control. M. J. Crowley, Jr. *Petrol. Engr*, 1951, **23** (8), C26–32.—The Wheatstone bridge conductivity cell can be used to measure in a simple way the amount of all dissolved solids in cooling-tower water to enable satisfactory control of composition. E. K. J.

691. Design of gasoline plants. Pt 1. Basic layout. O. L. Lewis. *Petrol. Engr*, 1951, **23** 10), C16–22.—The considerations affecting the layout of gasoline plants are: (1) safety; (2) economic construction; (3) convenient operation, and (4) easy maintenance. The basic factors on which the balance of these considerations depends are topography, rail and road location, prevailing winds, and climatic conditions. Insurance requirements are an excellent guide to the fulfilment of the safety considerations. Major design features, which affect layout, are: (1) method of cooling; (2) pump grouping; (3) instrumentation, and (4) possible expansion of the plant. The basic layout of two modern plants are analysed to show the influence of the above factors. E. K. J.

692. Design of gasoline plants. Pt 2. Equipment and unit layout. O. L. Lewis. *Petrol. Engr*, 1951, **23** (11) C5–13.—The basic considerations outlined in the first article are shown to apply in the equipment layout in each area of the plant. Details of the layout of compressor-plant process area, storage area, and utilities are analysed to indicate the balance between these primary considerations. The main points to be advantageously considered are adequate spacing between equipment and the symmetrical arrangement of equipment in the natural order of flow of the process. E. K. J.

693. Studies in fluidization. H. L. Olin and J. S. Patterson. *Petrol. Engr*, 1951, **23** (6), C5–12.—The fundamentals of fluidization are investigated with special reference to the effect of fouling on the behaviour of catalyst beds. The experimental bed is artificially fouled with materials likely to be encountered in practice, namely, petroleum

jelly, paraffin wax, pine tar, asphalt tar, and pine rosin. Plots of pressure drop against a modified Reynolds No. using particle dia in place of the dia of the capillary channel, shows similar characteristics to that in the quiescent region. Pressure drop for a given throughput decreases with increase of amount of fouling which indicates that decreased catalytic activity in commercial beds may be due partly to the isolation of the fouled particles by the diversion of circulating gas through large channels. The pressure drops through beds operating in the turbulent region are substantially constant for all degrees of fouling. Void factor and friction factor relationships are also plotted for clean round sand, fresh and regenerated catalyst. Ten useful references are given for following the development of fluidization technique. E. K. J.

694. New development in radiant heating. C. C. Tate. *Petrol. Engr*, 1951, **23** (6), C14–18.—Radiant cup burners have been installed in a simplified type of furnace in an attempt to obtain a more effective and cheaper source of heat on the refinery. Overall heater efficiency is 81·8%, and the excess air in the stack has been reduced to 9·2% with the possibility of further reduction. The economic advantage of this reduction is shown graphically. A totally inspirating type of cup-burner is also described which has operated satisfactorily even with prevailing wind velocities up to 40 m.p.h. Reduced maintenance, easy lighting, and uniform burning are advantages of this type of burner. The shape of the time–temp curve can be flexibly controlled, enabling high heat-transfer rates to be realized. E. K. J.

695. Short cuts in pilot-plant engineering. J. S. Rearick. *Mech. Engng*, 1951, **73** (12), 975.—It is desirable that pilot-plants should be scaled down from the proposed full-scale plant, but some compromise is inevitable, and close co-operation between process and mechanical designers is essential in order that process requirements are met in the final design. Continuity of supervision by one individual throughout design, fabrication, and erection, and co-ordination between the various departments eliminates the need for much unnecessary detail. Where extensive pilot-plant work is envisaged, standardized structural work in the pilot-plant area, the provision of permanent utility mains, and the development of standard details and designs prove economic. T. T.

696. Progress review No. 18 : Oil-burning equipment. G. J. Gollin. *J. Inst. Fuel*, Nov. 1951, **24** (140), 265.—Improvement of combustion efficiency of domestic burners by more careful design of air-admission devices has been made in the U.S. Work in Europe has covered the fields of boilers of heat input of 30,000 to 100,000 B.Th.U/hr and further development of the automatic burner.

In the field of burners for steam raising more efficient air registers have been produced and much higher atomizing pressures have been used. Several automatic devices for burners and some types of hybrid burners are also discussed. In America there has been rapid growth of " packaged heat."

Burners for industrial furnaces have been considered from the following aspects : small-capacity burners, high-intensity combustion, roof firing for continuous kilns, low-temp combustion, and gasifiers. In France the pressure-jet atomizer has been successfully used on horseshoe and cross-fired regenerative glass tanks. Application of modulated flame and high–low flame controls to industrial furnaces has been increased, as also has the use of photo-electric flame-failure safeguards. Small-capacity oil-burners have been successfully used in groups. Advances in America and England in low-pressure air-burners have led to the development of burners, in which over their operating range, the flame can be modified by the movement of a single control, the air/oil rates being practically constant. D. K.

697. Flare stack ignition devices. O. L. Clevenger and W. A. McElhannon. *Petrol. Engr*, 1951, **23** (5), C21.—The problem of lighting and maintaining the pilot light on flare stacks has been solved at Baytown refinery by installing an igniter adjacent to a pilot-light tube at the top of the stack. The igniter consists of a perforated tube into which a combustible mixture of natural gas and air is drawn by the natural gas supplied from the bottom of the stack and passes over a heating element, which is energized by a current of 60 amps at *ca* 6 V from a transformer, so that the element reaches a max temp of 1800° F in 20 sec. The combustible mixture is thus ignited, and the flame travels to the top of the stack to ignite the gas from the pilot tube. A thermocouple

at the top of the stack indicates whether the pilot light is burning. The advantages of this patented igniter are reduced explosion risks due: (1) to possible improper mixture of gas and air in ignition line, and (2) to absence of open flames or sparks at bottom of stack. Low-voltage heating reduces insulation difficulties associated with spark ignition. E. K. J.

698. Turbine governor mechanisms. J. A. Pellettere. *Oil Gas J.*, 27.12.51, **50** (34), 87.—No. 103 of the Refiner's Notebook series discusses four typical types of flyball governors, including mechanical, hydro-mechanical, and hydraulic (2). A figure shows the various mechanisms. G. A. C.

699. Skid-mounted gas cooler. D. H. Stormont. *Oil Gas J.*, 13.12.51, **50** (32), 107.—A unit designed to cool 2500 million cu. ft. gas daily from 115° to 85° F or within 10° F of wet-bulb temp is described. Unit is situated near Los Angeles for lowering water and condensable-liquid content of wet fuel gas to a point where it was marketable. G. A. C.

700. A dry seal gasholder. Anon. *Engineer*, 1951, **192**, 838.—This type of gasholder, developed in the U.S. for storage of pet vapours, has now been adopted for chemical process and industrial gases at pressures up to 20 inches w.g. First holder in this country, of 10,000 ft^3 capacity, was recently erected at Alston (Cumberland). Sealing medium used to prevent escape of gas through annular space between piston and shell of unit is flexible neoprene–asbestos cloth. Lowermost edge of seal is joined to piston, and uppermost edge to inner wall of holder shell about half-way up. As gas is pumped into holder piston rises and seal loops upwards, finally rolling off piston on to a telescoping fender without rubbing or abrasion. No roller guides or centring gear are required. Fabric seal has operating temp range from −40° to +180° F. A. C.

701. Centrifugal seal retaining assemblies. L. T. Ellis and C. L. Fussel. *Oil Gas J.*, 13.12.51, **50** (32), 100.—A serious and widespread weakness in mechanical seal installations has been found to exist on centrifugal pumps originally designed for soft packing. A bolting failure caused a large fire at a light-end plant of an Esso Standard Co. refinery; and a similar failure, resulting in a serious gas release, occurred at another refinery. Replacement of soft packing by mechanical seal without adequate engineering design may result in weaknesses in other plants.

Checking, redesigning, and modifying all seal-equipped pumps involves examination of bolts, bolt loads, and substitution of close-fitting bushing for auxiliary stuffing-boxes and glands in many instances. G. A. C.

702. Checking heat-exchanger performance. C. H. Gilmour. *Oil Gas J.*, 14.1.52, **50** (36), 99.—A method is described for computations in heat-exchanger design, which although involved in its development, is stated to be simple and accurate. Nine nomographs are given, and among them are included charts showing physical-properties factor for liquids in turbulent flow, mechanical design factors for various calculations, and a computation sheet on which are placed data obtained from the other eight nomographs.

A problem is stated and solution procedure given. G. A. C.

703. The rate of mixing of liquids in a propellor agitated mixing vessel. H. Kramers and W. H. Knoll. *Ingenieur*, 21.12.51, **63** (51), Ch. 67.—For the work described, a flat-bottomed, cylindrical mixing vessel 32 cm in dia, 50 cm high, and filled with dilute salt solution to a height of 32 cm is used. The stirrer is a three-bladed propellor 8 cm dia with a length along the axis of 2 cm and a pitch of 1 : 1. The rotational speed of the stirrer is capable of being varied between 400 and 2000 r.p.m. The rate of mixing is measured by injecting a concentrated salt solution and observing the time taken to reach balance on two cells of a Wheatstone bridge, the cells being located in the liquid, one above stirrer level and one below it at a position diametrically opposite. Results showed that the total number of revolutions required to obtain complete mixing (*i.e.*, to a variation of less than 0·1% in salt concentration) was independent of the rotational speed, and that this number reached a min when the axis of the stirrer was inclined.

Relatively rapid mixing was achieved by placing the stirrer appreciably off centre or by using a central mixer with four vertical baffles. R. K.

704. How to pack reciprocating rods against high pressures. W. Coopey. *Chem. Engng*, 1951, **58** (11), 164–6.—Practical points in the design of soft and metallic packings for high pressure are given. Many of the practices in the finishing of materials, running-in, lubrication, and design are shown to be wrong or pointless. D. H.

705. How to transfer volatile liquids under pressure. R. J. Sweeney. *Chem. Engng*, 1951, **58** (11), 153–61.—Movement of volatile liquids from one vessel to another can be achieved by pumping the liquid with or without a by-pass for the displaced vapour, or by pumping vapour if there is not sufficient liquid head available to avoid cavitation.

Equations are derived such that from the thermodynamic properties of the fluid the temp at any stage of the removal can be found.

The time taken to strip the tank down to a given pressure by evacuation can also be evaluated, and a numerical example shows that in removing liquid ammonia from a 10,000-gal tank car, 300 lb of vapour can be removed in 22 min, thus increasing the payload by 1%. D. H.

706. Sub-surface filling of drums. F. W. Langer and C. R. Irons. *Petrol. Process.*, 1951, **6** (12), 1382–4.—Details are given of a new device developed by Socony-Vacuum for more rapid filling of 55-gal lub.-oil drums. By filling from below the liquid surface, so thus avoiding foaming and enabling a higher pressure to be used, filling time for a particular oil has been reduced from 85 to 45 sec. The operation is further streamlined by automatic insertion and removal of the filling tube and automatic weighing. D. W. F.

707. Insulation and application methods for heated piping. Anon. *Petrol. Engr*, 1951, **23** (10), C44–6.—Details are given of the standard sizes of blanket and moulded types of insulation and description of the application of these two types for various purposes. Conditions to be considered in specifying insulation are temp, pipe dia, location, and degree of exposure. Recommended min insulation thicknesses are tabulated for both types for different pipe dia and temp. E. K. J.

708. Charts simplify refinery piping design. Anon. *Petrol. Engr*, 1951, **23** (7), C16–20.—Charts are given for determining the following functions for pipes of various materials operating at temp up to 1200° F: (1) pipeline expansion; (2) allowable combined bending and pressure stress; (3) longitudinal pressure stress; (4) number of plain U bends to absorb various expansions, and (6) anchor reactions in pipe. The results from the charts compare favourably with exact mathematical analysis, but the time required is greatly reduced. E. K. J.

709. Refrigeration in the petroleum industry. J. Charls, Jr. *Petrol. Engr*, 1951, **23** (4), C40–46; (5), C11.—The principles governing the choice of compressors, cooling systems, and refrigerants are surveyed in detail in Part 1. Concluding article contains descriptions of refining and petrochemical processes employing refrigeration, and compares the reciprocating and centrifugal compression systems of refrigeration with reference to the advantages associated with each system. E. K. J.

Distillation

710. Pressure-drop calculation in bubble-plate columns. J. C. Chu. *Petrol. Engr*, **23** (3), C9–16.—The importance is outlined of pressure-drop estimation in the design of bubble-plate columns and in the adaptation of existing columns for new purposes. There are four methods of computation of pressure drop at present available: (1) Rogers and Thiele consider separately the pressure drop: (*a*) through the riser; (*b*) through the slot opening, and (*c*) due to difference of liquid height between inside and outside of cap. Equations for slot-pressure drop are derived theoretically, and the first component can also be calculated. The third component will decrease with increased vapour flow, so that this analysis will yield max values. (2) Kirkbride's

formula, total pressure drop equals square of vapour velocity in riser multiplied by the density ratio of vapour to liquid, gives the appropriate order of magnitude of pressure drop for normally encountered vapour flow. (3) Eld's analysis divides the calculation into pressure drop due : (*a*) to riser and caps when plate is dry and (*b*) to foam and mist in space between plates which can be calculated as a function of amount, density, and distribution of liquid fed to a plate. (4) Dauphine's method considers : (*a*) pressure drop through a dry cap ; (*b*) the effect of liquid just covering the slots, and (*c*) the liquid head above the top of the slots. The dry cap pressure drop is further subdivided into (1) uptake, (2) reversal, and (3) slot-pressure drops, and all these quantities can be calculated by equations given in the paper. Seven cases of bubble-cap behaviour are discussed under various conditions and extended to give conclusions for the best construction of caps with min pressure drop. These are : (1) an uptake area of riser equal to annular area between riser and cap ; (2) a min riser height of $2\frac{1}{2}$ inches. The calculated results by each method are compared graphically. Nine graphs are plotted with different variables, and each show the characteristics of the different methods. Emphasis is laid on the advantage of Dauphine's method, which gives a realistic analysis of the variables affecting pressure drop. E. K. J.

711. Determination of hydrocarbon liquid–vapour equilibria. G. L. Farrar. *Petrol. Engr*, 1951, **23** (6), C41–47.—The calculation of liquid–vapour equilibria using Raoult's and Henry's laws is described with examples showing the application of the method to fractionation and absorption. For the latter case the use of the absorption factor "A" is explained. The article provides a useful introduction to the fundamental relations for the analysis of fractionating-tower performance. E. K. J.

712. The Wohl equation of state applied to the light hydrocarbons. K. A. Kobe and H .E. Von Rosenberg. *Petrol. Engr*, 1951, **23** (10), C35–8.—The Wohl equation uses three empirical constants evaluated from the critical constants of the gas, and is tested in this article by the calculation of ten pressures up to 1500 p.s.i.a. for six light hydrocarbons, viz. : the first five normal isomers of the paraffin series and *iso*butane ; and the gases nitrogen, water vapour, and carbon dioxide. Errors of the order of 1% are obtained for pressures below the critical pressure at all temperatures. For temperatures 50% above the critical the pressures may usually be calculated to within 1·5%, but greater error is obtained with the hydrocarbons. Generally, results are satisfactory for engineering purposes. E. K. J.

Absorption and Adsorption

713. New adsorption process recovers aromatics. Anon. *Petrol. Engr*, 1951, **23** (8), C21.—The Arosorb process as patented by Sun Oil Co. uses a new silica-gel adsorbent to concentrate benzene, toluene, and xylenes from distillates. Two desorbents, butane and mixed xylenes, are used to remove the saturates and aromatics from the liquid and adsorbed phases of the silica gel respectively, after the feed stock has been treated. Aromatics and saturates are subsequently recovered by distillation. The process operates on a cycle of *ca*100 min, which is automatically controlled by refractive-index measurement of the effluent streams, which causes the saturate and aromatic-product lines to be switched. E. K. J.

Solvent Extraction and Dewaxing

714. Udex gives sharp cuts. Anon. *Chem. Engng*, 1951, **58** (11), 242.—Extraction of benzene, toluene, and xylene from reformed naphthas with diethylene glycol is expected to provide in the U.S.A. 1·5 million gal p.a. by Dec. 1952.

The advantages are that a wide range of feed stocks can be used and solvent recovery by distillation is simple.

Some details of the process are given. D. H.

Cracking

715. Chemists survey oil refining technology. A. L. Foster. *Petrol. Engr*, 1951, **23** (10), C3.—A survey of the chemical processes involved in present-day oil refining

as presented at the Petroleum Division of the American Chemical Society, New York, Sept. 1951, gives technical details of: (1) olefin polymerization by thermal and calalytic reforming and fluid hydroforming and (2) hydrocarbon synthesis. It is estimated that 60% of gasoline made in the U.S.A. is composed of molecules not present as such in the original crude; this emphasizes the importance of the above processes. Details are given of operating conditions: (1) temp; (2) pressure; (3) space velocity of charge, yields, O.N.'s of products, and cost data of plant. Two theories of polymerization, depending on the formation of an ester and carbonium intermediate respectively, are outlined. E. K. J.

716. How Gulf Oil built a 63,000 barrel cat cracker in less than a year. F. L. Resen. *Oil Gas J.*, 13.12.51, **50** (32), 78.—A description of the world's largest catalytic cracking unit of its type erected at Port Arthur, Texas, is given.

The cracker is largely self-contained, and the motor-gasoline output of the refinery has been stepped up to 20,000 b.d. without change in crude throughput.

A flow diagram is provided. G. A. C.

717. New design features in catalytic cracker. H. K. Wheeler. *Petrol. Engr*, 1951, **23** (10), C5–10.—The 7000-b.d. fluid catalytic cracking unit at El Dorado, Arkansas, is completely heat balanced in operation, as all heat required to complete the reaction is supplied by combustion of the coke so that neither recycle catalyst coolers nor preheat furnace are required. Emphasis has been placed on: (1) simplified design of units to reduce installation and operating cost and (2) open layout to facilitate inspection and maintenance. The reactor of the catalyst plant surmounts the regenerator to eliminate an elevator. Transfer of catalyst back to reactor is by means of air pressure, and fresh catalyst is introduced by vacuum from a steam ejector. The highest operating level is kept to a minimum elevation, and most of the process control is possible from the lowest levels. Other details of operation and mechanical construction of the plant are described in adequate manner. E. K. J.

718. Factors affecting throughput in catalytic cracking. P. M. Reynolds. *Petrol. Engr*, 1951, **23** (10), C47–52.—An introductory survey of the catalytic cracking processes describes the fixed-bed, Thermofor, and fluid type of units. Essentially the cracking reaction is the same for each type, and the basic difference is in the heat balance. The factors analysed are those associated with: (1) the catalyst; (2) heat balance; (3) catalyst reactions, and (4) regeneration of catalyst—the last factor is usually the limiting one in the throughput of a unit. The three functions of catalyst are: (1) reaction catalyser; (2) heat-transfer medium from generator to reactor, and (3) coke-handling medium. E. K. J.

719. Thermal cracking. H. R. Linden. *Petrol. Process.*, 1951, **6** (12), 1389–96.—Experimental data obtained from the severe cracking of various oils for the production of gas in a laboratory unit are presented. Partial-pressure constants for the gaseous paraffins, unsaturates, and hydrogen formed are given for pressures of 1 to 4 atm, temp from 1450° to 1600° F, residence times of 1 to 14 sec for oils ranging from natural gasoline to Bunker C fuel oil. Empiricial relationships are presented for the estimation of gaseous-product distribution in inert, or hydrogen-containing, atmospheres, as a function of the C/H ratio of the feed, residence time, partial pressure of the oil gas, cracking temp, and hydrogen-to-oil feed ratio. Solution for the paraffin to unsaturates ratio is aided by a nomograph. Fifteen references. D. W. F.

720. Catalytic upgrading by Hydroforming. H. G. McGarth. *Oil Gas J.*, 27.12.51, **50** (34), 78.—Hydroforming reactions, fluid-catalyst effect of operating variables as indicated by pilot-plant data, and fluid hydroforming economics are discussed.

A flow sheet of a commercially operated process is given, and among the ten tables provided are those showing catalyst activity tests, fluid hydroforming with MoO_3–Al_2O_3 catalyst on various naphthas and O.N.s. G. A. C.

721. Midget cracker helps big brother. C. K. Viland. *Petrol. Process.*, 1951, **6** (12), 1370–3.—A midget fluid cat cracking unit used by the Tide Water Associated Oil Co. is described. It has proved useful in examining process variables and in the com-

parison of feed stocks and catalysts. Proper evaluation of these factors has greatly improved throughput and gasoline productivity of the company's cat cracker at their California refinery. The type of research carried out on the unit is reviewed and some typical data from recent investigations are included. D. W. F.

722. Continuous contact coking for processing Alberta bitumen. E. R. Smoley and A. H. Schutte. *World Petrol.*, 1951, **22** (13), 36–8.—Contact coking process is briefly described and data for a semi-commercial plant running 4 gravity Wilmington (Calif) asphalt of 14 pen and 150° F R. & B. m.p. show that once-through yields of about 25% C_4 to 400° F material were obtained. Debutanized gasoline base had O.N. (research) 78 to 83 clear and 88 to 92 with 3 cc T.E.L. In a discussion following the paper it was estimated that a plant handling 10,000 b.d. heavy charge would cost \$1·5 to \$2·0 million and 35 to 50 cents/b.d. direct operating costs. Fuel consumption was put at 5% of charge. Coke pellets, $\frac{1}{2}$ to 1 inch dia containing 3% volatiles, would probably be suitable for power-generation schemes. E. B.

723. Kinetics of regeneration of alumino-silicate catalysts. G. M.Panchenkov and N. V. Golovanov. *Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk*, 1951, 1513–21.—Description and diagram are given of laboratory equipment used for studying heterogeneous reaction of oxidn of cat coke. Cat particles, coated with coke (approx 5%), are suspended in reaction tube from spring balance (sensitivity 2×10^{-4} g); average weight of granules was 6×10^{-1} g. Cat is heated in stream of inert gas to remove volatiles and air introduced when test temp is attained. Five different synthetic Al–Si cat were studied. Coking was by cracking of gas oil (d_4^{20}, 0·863, I.B.P. 245° C, 90% vol at 360° C, paraffins 91·6%, aromatics 8·4%) at 475° C. Separate test showed absence of coke migration on cat surface. Rate of oxidn (as shown by loss in wt of cat particle) increases with air flow up to limiting value of latter, difference between oxidn rate at various temp is less marked at low air flow. Up to approx 470° C oxidn rate is slow and similar for all cat, above this temp individual differences appear. Difference in oxidn rate with cat particle size is evident only at temp >500° C. Most tests were carried out with hourly air-flow rate of 300,000 vol air/vol cat. At high temp (>520° C) relative rate of oxidn decreases with increasing coke content of cat. Plot of log relative reaction rate against reciprocal of abs temp is for most cat linear below approx 540° C. Kinetic aspects of the experimental results are discussed; at oxidn <520° C process is within inner kinetic region and has an activation energy (for four of the cat) of 31,000 cal/mol, above this temp oxidn proceeds in inner diffusion region. Limiting values of temp and coke content at which change from kinetic to diffusion region occurs are of same order for all cat. V. B.

Alkylation

724. Sulphuric acid alkylation for gasoline. J. W. Jewell, Jr., and C. C. King. *Petrol. Engr*, 1951, **23** (5), C24–30.—A new cascade mixer reactor for alkylation is described in which contact between *iso*butane, olefin, and sulphuric acid takes place in separate zones. Feed is supplied to each zone, but the acid and *iso*butane cascade from zone to zone so that the *iso*butane–olefin ratio is maintained at the highest possible level in each zone. The reduction of the external *iso*butane–olefin ratio required, results in a decrease in cost of the *iso*butane-recycle equipment, which is one of the most costly features of alkylation. Another advantage of the process is the reduction of power requirements for circulating emulsion to less than 25%. The analysis of results of process operation show that: (1) greater yields of alkylate of higher octane rating are obtained; (2) side reactions are reduced, and (3) a better economic balance is obtained. The combination of this process with catalytic polymerization results in economy of debutanizing capacity. The economics of a simplified acid-recovery system are analysed and indicate that the acid charge is potentially eliminated as a significant factor in the cost of the alkylation process. E. K. J.

725. Alkylation plant improvements. D. H. Putney. *Petrol. Engr*, 1951, **23** (6), C27–35.—With hydrofluoric acid alkylation it was found that the reaction time was 8 to 10 min instead of the design figure of 20 min, and in order to use the increased available capacity of the contactors, more efficient heat removal was accomplished by

replacing finned-tube bundles by U-tube bundles. The heat-transfer rate was increased more than threefold. A consequent reduction of reaction temp is possible, depending on the balance between the throughput and cooling capacity increases. New contactors incorporating the improved tube bundles have been designed to operate in a horizontal position resulting in decreased erection costs.

With sulphuric acid alkylation, which requires refrigeration due to the low reaction temp, the U-tube bundle reduces the load on the refrigeration system. The operation of a number of contactors in series and discharging into separate settlers results in increased O.N.s and yields of alkylate due to the improved effect of higher concentration of acid in the early stages. The principle of effluent refrigeration increases the *iso*butane–olefin ratios by using the hydrocarbon from the settler as refrigerant, and evaporation of *iso*butane from effluent effects the cooling in the reactor. This reduces the load on the de-*iso*butanizer tower.

A two-stage alkylation process is being developed in which olefins are first absorbed in recycle acid. Possible advantages are the increased availability of olefinic feed stocks and improvement of alkylate product from existing feed stocks. E. K. J.

Chemical and Physical Refining

726. Industrial petroleum chromatography. (3). H. Weil. *Petroleum*, Jan. 1952, **15** (1), 9–12.—The part of an article reviewing history and technology of industrial petroleum chromatography for the period, 1914–34. (See Abs. 1435—1951 and 188—1952.)

The origins of silica gel and its properties which made this material so useful in petroleum fractionation are surveyed, and typical examples are given of the chromatographic fractionation of hydrocarbon mixtures during the period. A description of the first separation of a coal-tar solution is included, showing what delicate separations could be effected and that very minute amounts of constituents could be spatially concentrated.

A brief review of the equipment designed for adsorption refining of petroleum and petroleum products is given, and is stated to have decidedly influenced chromatographic engineering.

107 references are given for both Pts 1 and 2. R. E. P.

Special Processes

727. New petrochemicals plant producing full range of products from Middle East naphtha. H. E. Charlton. *Oil Gas J.*, 20.12.51, **50** (33), 201.—The chemicals from petroleum plant owned by Petrochemicals Ltd., Manchester, is described, and a simplified chart of operations given.

The plant consists of an integrated group of units for the separation, purification, and conversion of the products arising from the five Catarole cracking units which produce liquid and gas products from petroleum naphtha. G. A. C.

728. Benzene from petroleum. Anon. *World Petrol.*, 1951, **22** (12), 72–7.—Growth in demand for benzene is exceeding increase in production from non-pet sources. Increasing number of cat reforming processes are being brought into operation for aromatic production. Arosorb and Udex processes for separating aromatics from reformate have been introduced. In Arosorb process reformate is introduced into a column of silica gel wet with xylenes. Benzene and toluene in the reformate displace free and adsorbed xylene, which flows out mixed with saturated components of reformate. When the gel is saturated with benzene and toluene, butanes are injected to wash out remaining saturates. Adsorbed aromatics are then displaced by xylenes, thereby completing the cycle of operations. The various products are separated by dist. Udex process employs a glycol–water mixture as solvent in an extraction process. The solvent has high selectivity and good solvent properties for aromatics, and is immiscible with aromatic–paraffin mixtures in the entire range of aromatic concn. Selectivity and solubility may be varied by adjusting water content, and are almost independent of temp, thus enabling extraction to work at stripper reboiler temp. Simplified flow diagrams of both processes are given, with data on products. Removal of benzene does not seriously affect O.N. of reformate. E. B.

729. Desalting crude oil. A. L. Foster *et al.* *Petrol. Engr*, 1951, **23** (8), C34.—A survey of desalting systems is presented to show the advantages which are combined in the Howe-Baker desalting unit. In this unit water and caustic are added to the crude to remove the salt and then demulsifiers are added, which, with the use of a 16,000 A.C. voltage, separates the oil and water phases to give *ca* 80% salt removal. E. K. J.

730. New adsorption processes for gas dehydration. L. L. Laurence and L. S. Reid. *Petrol. Engr*, 1951, **23** (3), C25–30.—The numerous difficulties encountered by the scaling-down of large dehydration processes using solid granular adsorbent led to the design of two types of units for service on individual wells and on transmission lines respectively. In the former case throughputs of 3 to 5 million cu. ft. of gas per day must be handled at pressures of 2000 p.s.i. and higher, but in the latter case emphasis laid on the minimizing of pressure drop. Both units can increase their capacity by mixing dried gas with gas which has only been separated, to give a gas of sufficiently high dew point. The operation can be made fully automatic to give gas of controlled dew-point, but attention must be given to ensure that the valves on the cycle system change position successively, to prevent attrition of dessiccant by possible instantaneous flow reversals. E. K. J.

Metering and Control

731. The instrument department grows up. R. F. Angell and R. Tobi. *Petrol. Engr*, 1951, **23** (6), C23–6.—The increased use of instruments in the refinery has resulted in the development of specialized techniques for their installation and maintenance. This growth of instrumentation has brought problems of accuracy, standardization, stocks of spares, and records, the answers to which are given in the article. The value of preventive maintenance is emphasized, but the schedule of maintenance for different refinery components must be planned on the basis of experience. E. K. J.

732. Instrumentation for boilerhouses and oil refineries. J. A. Pellettere. *Industr. Engng. Chem.*, 1951, **43** (12), 2704–5.—Use of product quality analysers is stated to be unjustified in oil refineries and unnecessary in boiler-houses. Specialized equipment, when available, would be used in refineries after favourable investigation of the economics involved. E. J. C.

733. Differential head meters useful to the petroleum industry. H. S. Bean. *Petrol. Engr*, 1951, **23** (11), C15–20.—The characteristics are described of seven types of differential head meters, viz.: (1) venturi tube; (2) flow nozzle; (3) thin-plate square-edge orifice; (4) tapered tube and plug; (5) elbow; (6) gentile flow tube; (7) friction flow. In each case the advantages and disadvantages are balanced. In addition, the problems of installation and range of flow rate are discussed for the first three types of meter. Brief mention is made of the factors influencing the choice of secondary elements required to measure the differential pressure produced by the above types of primary elements. E. K. J.

734. Unbalanced force reactions in control valve plugs and their influence on diaphragm motor design and operation. Pt 2. R. A. Rockewell. *Petrol Engr*, 1951, **23** (3), C17–24.—(*See* Abs. 2662—1951.) The first article described the characteristics of single- and double-seated parabolic plugs. In the concluding one tests on the following types of plugs are described and results plotted as net stem force against valve lift: (1) V port, both single- and double-seated; (2) quick-opening, both single- and double-seated; (3) special overlapping quick-opening, single-seated, and (4) single-seated special cup-shaped. The results of these tests are then applied to the operation of (1) spring-loaded and (2) springless diaphragm motor valves, and, the behaviour is analysed for single-seated parabolic plugs of each type of diaphragm: (*a*) when the flow is over the seat tending to close and (*b*) when the flow is under the seat tending to open. The travel characteristics for both types of diaphragm are shown graphically as diaphragm air pressure against % valve lift for flows under and over the seat. The

use of double-seated valves, with both types of diaphragm, is discussed on the basis of : (1) the analysis of single valve tests ; (2) actual results of double-seated valves, and (3) their application with diaphragm motors. E. K. J.

735. Refinery instruments. What makes them tick? Pt 6,—Controllers. C. E. Shannahan. *Petrol. Process.*, 1951, **6** (12), 1374–9.—The operation of air-actuated controllers is lucidly explained by reference to diagrammatic views of the controller set-up and practical examples of use. The controller types described are on–off, proportional, reset proportional, derivative, and proportional-reset-derivative. D. W. F.

736. Quality control in the process industries. J. G. Dobson. *Industr. Engng Chem.*, 1951, **43** (12), 2695–700.—Application of standard instruments can often lead to adequate quality control in industrial processes without recourse to more expensive equipment such as spectrographs. Suitable methods of continuous control are described by reference to the physical–chemical properties on which the measurement depends. The examples given include the use of a differential-pressure transmitter, to compensate for changes in feed stock, on an *iso*butane-*n*-butane fractionating unit. E. J. C.

737. Selection of electric motor control. J. Benish. *Petrol. Engr*, 1951, **23** (7), C5–10.—The satisfactory operation of motors in a refinery depends on the proper choice of controls. The basic types of control circuit are described for the starting, stopping, and reversing of A.C. and D.C. motors, and methods of protection are outlined for overload and short-circuit conditions. The uses of actuating devices for the automatic control of motors are tabulated, and methods are given for the amplification of signals provided by these devices. E. K. J.

Products

Chemistry and Physics

738. Chemistry of the surface and the activity of alumina–silica cracking catalyst. M. W. Tamele. *Disc. Faraday Soc.*, 1950, **8**, 270–9.—Alumina–silica cat is an amorphous material prepared by pptn of alumina from an Al salt in the presence of excess silica hydrogel, to give about 10% alumina in the product after calcining at 500° C. Cat owes its activity to a number of acid sites on the surface formed by condensation of surface OH groups of incompletely polymerized silica hydrogel with those of the hydrolysed Al ions. Acid strength of the surface has been shown to be in range of strong acids known to promote hydrocarbon reactions. A linear relationship was found between activity of the cat for polymerization of propylene at 200° C and the number of acid sites in the surface determined by titrating the solid in suspension in benzene, with *n*-butylamine using *p*-dimethylaminoazobenzene as indicator. The cracking of *iso*propylbenzene at 500° C appeared to be proportional to the square root of number of acid sites. E. B.

739. Some notes on oxide catalysts for dehydrocyclization. H. Steiner. *Disc. Faraday Soc.*, 1950, **8**, 264–70.—Cat involved belong to periodic sub-groups 4, 5, and 6, with the exception of CeO_2. Active centres catalysing dehydrogenation, cyclization, and isomerization (the three steps involved in dehydrocyclization) are shown to be largely identical. Kinetic studies of cyclization of paraffins proceeding according to the scheme paraffin ⟶ olefin ⟶ aromatic have shown, in case of *n*-heptane, that the olefin is present in stationary concn and that the ratio of cyclization to dehydrogenation alters only to a minor extent for a fourfold decline in cyclization rate. Isomerization also takes place simultaneously with cyclization. In discussing the structure of oxides supported on γ-Al_2O_3, which is itself inactive, it is suggested that the appreciable vapour pressure of molybdenum trioxide at 600° C (0·1 mm Hg), compared with the extremely low value for Cr_2O_3, may account for their differences ; the former oxide being spread out in a monolayer, the activity of which is constant until the monolayer is complete, in contrast to Cr_2O_3 cat, which appears to form clusters, the activity of which declines in proportion to their growth, activity being assessed on unit weight of catalytically active oxide. E. B.

740. Vapour phase oxidation of hydrocarbons. I. Aldehydes, ketones, and acids produced during the low temperature oxidation of *n*-heptane and methyl*cyclo*hexane. F. H. Garner and D. S. Petty. *Trans. Faraday Soc.*, 1951, **47**, 877–84.—In oxidn of *n*-heptane at 250° to 400° C carboxylic acids, principally acetic, appear to be formed by a process other than direct oxidn of aldehydes, and not all the formaldehyde is formed by a stepwise degradation of higher aldehydes. Aldehydes and ketones are mainly of high mol. wt. It is suggested that formaldehyde arises from the homogeneous gas-phase decomposition of an alkyl hydroperoxide ROOH $\longrightarrow$ H.CHO competing with the surface reactions ROOH $\longrightarrow$ R_1.CHO or ketone. Methyl*cyclo*hexane was oxidized at 325° to 400° C.

II. Formation of unsaturated hydrocarbons during the low-temperature oxidn of *cyclo*paraffins and paraffins, *ibid.*, 884–9.—Olefins were determined in the oxidn products of *n*-heptane, *iso*-octane, and methyl*cyclo*hexane with an accuracy such that vol-% determined = true vol-% $\pm$ 0·15%. A low temp max of olefin formation was observed for vapour-phase oxidn of the hydrocarbons, which was attributed to alkyl radical breakdown. Alkyl radicals formed during the oxidn of *iso*-octane appear to be more unstable than from methyl*cyclo*hexane and *n*-heptane, resulting in greater olefin formation per reacting mol of hydrocarbon.

III. Comparison of the oxidn of methyl*cyclo*hexane and *n*-heptane, *ibid.*, 889–96.—There is a min in the oxidn rate of *n*-heptane and methyl*cyclo*hexane between 400° and 500° C, the rate of the latter being much lower. This is explained on the assumption that the increase of temp results in increasing instability of peroxide radicals and hence decrease in formation of peroxide molecules. In the case of *n*-heptane the products resulting from peroxide radical decomposition are more likely to participate in further reaction than those from methyl*cyclo*hexane oxidn because of the greater stability of peroxide radicals from *tert*- and *sec*- CH bonds of the *n*-heptane relative to quaternary CH bonds postulated for peroxide radicals from methyl*cyclo*hexane. At 500° C cracking is believed to compete with oxidn and so account for the decrease in O_2 consumption per mol of hydrocarbon. E. B.

741. Vapour phase oxidation of hexanes. E. J. Kahler, A. E. Bearse, and G. G. Stoner. *Industr. Engng Chem.*, 1951, **43** (12), 2777–81.—Apparatus and experimental procedure for vapour-phase oxidation of *n*-hexane, 2 : 3, dimethyl-butane, and 2 : 2-dimethylbutane are described. Considerable differences were observed in the case of oxidation of the isomeric hexanes and in the nature of products formed under different conditions. Oxidation of *n*-hexane under precool-flame conditions at 280° C resulted in relatively stable organic peroxides and little hydrogen peroxide. At higher temp (480° C) the main products were unstable mixtures of hydrogen peroxide and formaldehyde. Oxidation of the other hexane isomers was slight even at 480° C.

E. J. C.

742. Catalytic dehydrogenation of ethyl naphthalene. J. C. Ghosh and S. Rama Das Guha. *Petroleum*, Feb. 1952, **15** (2), 33–4.—The dehydrogenation of β-ethyl naphthalene to styrene has been studied at atmospheric pressure using various catalysts and elevated temperatures. Catalyst A (Cr_2O_3 (70%),Al_2O_3 (15%), and Cu (15%)) yielded 36·5% β-vinyl naphthalene at 600° C. β-ethyl naphthalene diluted with carbon dioxide in the ratio 1 : 2 (mols) gave a constant yield of 35% styrene at 600° C over the catalyst B (Cr_2O_3 (80%), Al_2O_3 (15%), Fe_2O_4 (15%).

Data are also presented for the chemical equilibrium at pressures between 10 and 40 mm and in the temp range of 360° to 510° C, using catalyst A. Equations are given for the heat of reaction, free energy change, entropy change, and for the equilibrium constant. R. E. P.

743. Physical and chemical adsorption of long chain compounds on radioactive metals. F. P. Bowden and A. C. Moore. *Trans. Faraday Soc.*, 1951, **47**, 900–8.—Using as the adsorbing surface, 0·001-cm-thick metal foil, a few cm^2 in area and previously irradiated with neutrons, it is shown that no chemical reaction occurs between Pt and Au and stearic acid, ethyl stearate, and octadecyl alcohol. Adsorption of stearic acid, and to a lesser extent ethyl stearate, on Zn, Cd, and Cu is followed by soap formation, the soaps being physically attached to the surface. In the presence of the adsorbate, relatively thick layers of soap may be built up. Results are correlated with electron-diffraction studies and lubricating properties of the acid, alcohol, and ester. E. B.

744. Synthesis of polyacetylenic compounds. E. R. H. Jones, M. C. Whiting, J. B. Armitage, C. L. Cook, and N. Entwhistle. *Nature*, 1951, **168**, 900–3.—Syntheses and properties of the dimethyl poly-ynes $CH_3(C{\equiv}C)_nCH_3$ (I), where $n = 2$ to 6, the diphenyl poly-ynes $Ph(C{\equiv}C)_nPh$ (II), where $n = 3, 4, 6, 8$, and the glycols

$$Me_2C(OH)(C{\equiv}C)_nC(OH)Me_2 \text{ (III)},$$

where $n = 2$ to 6 are described.

The compounds I are crystalline solids which (except $n < 4$) decompose below their m.p. They are stable in the dark, but storage at $-70°$ is desirable. Compounds III are also crystalline solids (except $n = 6$) and are more stable than I. Compounds II are red solids which vary in stability; $n = 6$ is quite stable, $n = 8$ is unstable even in the dark.

Compounds of the formula $MeCH{=}CH(C{\equiv}C)_nCH{=}CHMe$ ($n = 2, 3, 4$), and the acids $Me(C{\equiv}C)_nCOOH$ and $HOOC(C{\equiv}C)_nCOOH$ ($n = 2, 3$) have also been prepared.

Details of the absorption spectra between $\lambda = 2000$ and 4000 Å are given.

H. C. E.

745. A mechanism of intense gaseous combustion. A. H. Howland and W. A. Simmonds. *J. Inst. Fuel*, Nov. 1951, **24** (140), 252.—Experiments on the combustion of a premixed supply of air and gaseous fuel inside a refractory tube are described. The combustion occurs in a series of explosions. Fresh mixture flows in, driving out the products of the previous explosion. This mixture is ignited due to radiation and convection from the walls, turbulent mixing with combustion products, and mixing of active species from these products. The whole mixture then explodes, the explosion does not travel along into the fresh mixture, due to cooling in the cold, narrow inlet tube. The limits on the further development of this type of combustion, to give more rapid rates of heating, appear to be the supply pressure for the mixed fuel and the length of the tube required to give satisfactory operation. Noise produced by the burner cannot be eliminated, but it can be reduced by selecting a tube length which does not resonate to the frequency produced by the burner. Further investigations are being made. D. K.

746. Combustion in bunsen flames. F. R. Caldwell, H. P. Broida, and J. J. Dover. *Industr. Engng Chem.*, 1951, **43** (12), 2731–9.—An apparatus is described for investigating mechanisms of combustion processes, which has been used to determine apparent flame speeds and line-reversal temperatures of methane–air mixtures at atmospheric pressure. Effects of water vapour, gas velocity, and nozzle temp on flame speeds were also determined.

A brief description is given of a spectroscopic apparatus for determining rotational temperatures and concentration of free radicals. E. J. C.

747. Kinetics of combustion.—Relation to emission flame spectroscopy. K. J. Laidler and K. E. Shuler. *Industr. Engng Chem.*, 1951, **43** (12), 2758–61.—An investigation was carried out to determine the usefulness of the spectroscopic study of flames in studying combustion processes. In the case of carbon monoxide these spectroscopic investigations have yielded enough information to permit a more detailed discussion of the combustion mechanism. Much more work has to be done, both theoretically and experimentally, before this useful method can be fully used in studying combustion kinetics. E. J. C.

748. Preflame combustion of hydrocarbons. J. R. Thomas and H. W. Crandall. *Industr. Engng Chem.*, 1951, **43** (12), 2761–3.—An U.V. spectrophotometer was employed to study the kinetics of hydrocarbon combustions. The rate of formation of formaldehyde gradually increased during the induction period, and there was a rapid production of formaldehyde during the cool flame. An absorption peak was found at 2600 Å for *n*-butane and higher hydrocarbons, but not for *iso*butane and propane. Although no reference is actually made in the paper to the compound by name, it is inferred in the summary that this absorption peak is due to β-dicarbonyl compounds. E. J. C.

749. Preflame combustion of hydrocarbons—identification of β-dicarbonyl compounds. M. R. Barusch, H. W. Crandall, J. Q. Payne, and J. R. Thomas. *Industr. Engng Chem.*, 1951, **43** (12), 2764–6.—The experimental procedure and discussion involved in establishing the identity of β-dicarbonyl compounds is reported (cf. Abs. 748). E. J. C.

750. Preflame combustion of hydrocarbons—possible intermediates to β-dicarbonyl formation. M. R. Barusch, J. T. Neu, J. Q. Payne, and J. R. Thomas. *Industr. Engng Chem.*, 1951, **43** (12), 2766–9.—Tendencies of *n*-butyraldehyde, methyl ethyl ketones, 1-butene, 1 : 3-butadiene, crotonaldehyde, and methyl vinyl ketone to produce a β-dicarbonyl compound in preflame reactions were measured by an experimental procedure which is described. *n*-Butyraldehyde and methyl ethyl ketone do not contribute towards β-dicarbonyl formation, and the other compounds mentioned may not be significant as intermediates. A possible mechanism, and some evidence to support it, is put forward to explain β-dicarbonyl formation. E. J. C.

751. Fundamental flame velocities of hydrocarbons. M. Gerstein, O. Levine, and E. L. Wong. *Industr. Engng Chem.*, 1951, **43** (12), 2770–2.—Flame velocities of a series of alkadienes and *cyclo*-alkanes were determined to find the effect of molecular structure on flame velocity in 25-mm borosilicate glass tube. E. J. C.

752. Partial combustion of methane with oxygen. R. Mungen and M. B. Kratzer. *Industr. Engng Chem.*, 1951, **43** (12), 2782–7.—The effect of oxygen–CH_4 ratio on the conversion of methane, the final temp, carbon efficiency, oxygen efficiency, and hydrogen–carbon monoxide ratio, were determined at 300 p.s.i.g. for the partial combustion of methane in a pilot plant. Effect of preheat temp and space velocity was also determined. Results, which are tabulated and plotted, indicate the feasibility of the process for supplying feed gas for hydrocarbon synthesis. E. J. C.

753. Flame radiation research joint committee : reports of 1949 trials at Ijmuiden. Various Authors. *J. Inst. Fuel*, Nov. 1951, **24** (140), Supplement.—A series of papers is presented representing the first year's work of the Flame Radiation Research Joint Committee. The papers are entitled : " Purpose and plan of the experiments," by J. E. de Graaf and M. W. Thring. " Review of previous work on luminous radiation," by F. M. Comerford. " Heat-flow meters," by R. T. Fowler *et al.* " Total radiation pyrometers," by E. J. Burton *et al.* " Suction pyrometry," by I. M. D. Halliday. " The main experiments," by R. Mayorcas, and " Control and instrumentation of the experimental furnace," by G. W. Stein Callenfels. D. K.

754. Flame propagation. D. M. Simon. *Industr. Engng Chem.*, 1951, **43** (12), 2718–21.—A discussion of the active particle diffusion theory of flame propagation based on recent published data on flame velocities. Calculations based on the latter data indicate that max flame velocities are consistent with an active particle mechanism of flame propagation. Data given include burning velocities of fifty-six hydrocarbons. E. J. C.

755. Hydrocarbon flame spectra. G. A. Hornbeck and R. C. Herman. *Industr. Engng Chem.*, 1951, **43** (12), 2739–57.—Hydrocarbon flame spectra have been examined over the range ~2,000 to ~9000 Å so that the identity of band systems under a variety of flame conditions could be established. The required techniques are described, and results are presented in the form of densitometer tracings of bands, obtained under a wide variety of oxygen–fuel ratios. E. J. C.

756. Electrical properties of flames. H. F. Calcote and R. N. Pease. *Industr. Engng Chem.*, 1951, **43** (12), 2726–31.—The effect of longitudinal electric fields on bunsen-burner flames was studied for *n*-butane–air mixtures. A platinum ring on the outside of the quartz burner tube was made positive or negative with respect to a brass burner inside the quartz tube. For a field (ring positive) up to 16 kV : (1) the composition limits of flame stability can be increased by as much as 200% ; (2) the composition limits of flame stability reach a saturation point at the order of 2 kV ; (3) the range of flow rates for burner–flame stability can be increased by 100% ; (4) dead space can be reduced by 30% ; (5) flame pressure can be increased by more than 100%. With the ring negative to 16 kV, the general trends were as for the ring positive, but certain irregularities were observed. For example, dead space is increased and then suddenly decreased with increasing −ve field.

A mechanism is proposed to explain the effects based on the existence of large numbers of ions, which do not appear to play a significant role in the combustion process. E. J. C.

757. Flammability limits of hydrocarbon air mixtures. J. T. Di Piazza, M. Gerstein, and R. C. Weast. *Industr. Engng Chem.*, 1951, **43** (12), 2721–5.—A detailed study of the effect of molecular structure on the flammability limits of pure hydrocarbons at reduced pressures. The apparatus and experimental procedure are described, together with a discussion on the experimental variables. The low-pressure limit of propagation of 34 mm Hg was practically unaffected by mol. wt., branching, or unsaturation. Limit curves of pressure *v.* fuel concentration were characterized by a two-lobe form.
E. J. C.

758. Recent advances in organic fluorine chemistry. R. N. Haszeldine. *Nature*, 1951, **168**, 1028–31.—$CF_3(CF_2)_nCOOAg$ (I) and $AgOOC(CF_2)_nCOOAg$ (II) react with halogens (X_2) to give $CF_3(CF_2)_nX$ and $X(CF_2)_nX$ as the main product, but small amounts of esters and lactones are also obtained. Thus I ($n = 0$ or 2) also yields CF_3COOCF_3 or $C_3F_7COOC_3F_7$; and II ($n = 3$ or 4) yields $O(CF_2)_3CO$ or $O(CF_2)_4CO$.

These compounds are believed to arise by free radical mechanisms. With aqueous reagents the lactone ring opens to give unstable compounds with the CF_2OH group, which loses fluorine as $2F^-$.

Perfluoro olefins can be prepared from the corresponding paraffin or silver salt of the acid by reaction with zinc. $CF_3CF{=}CF_2$ is obtained by heating I_2 and C_3F_7COONa.

Grignard reagents $CF_3(CF_2)_nMgI$ are prepared in dilute anhydrous solution at a temp between $-40°$ and $-80°$ C; they react similarly to hydrocarbon Grignard reagents. On standing they decompose to $CF_3(CF_2)_nH$, $CF_3(CF_2)_{n-2}CF{=}CF_2$, MgF_2, MgI_2, and small amounts of $CF_3(CF_2)_{2n}CF_3$. Reaction mechanisms are proposed to account for these products. Grignard reagents have also been used to prepare carbinols, *e.g.*, $(CF_3)_2CHOH$ and $(CF_3)_3COH$.

Perfluoro acids of the type $CF_3(CF_2)_nCOOH$, $HOOC(CF_2)_nCOOH$ can also be prepared by means of Grignard reagents. The acids $H(CF_2CF_2)_nCOOH$ are prepared from the corresponding iodide or from CH_3OH and $CF_2{=}CF_2$ via the alcohols

$$H(CF_2CF_2)_nCH_2OH.$$

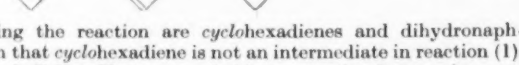
The interaction of hexaiodobenzene and I_2F_5 yields perfluoro*cyclo*hexyl iodide $C_6F_{11}I$ (III), which can be converted via the Grignard reagent and CO_2 to $C_6F_{11}COOH$. C_6F_{10} is also formed from decomposition of the acid in aqueous solution. III reacts with acetylene to give $C_6F_{11}CH{=}CHI$.

The possibility of preparing perfluoro silicones is discussed. Perfluoro alkyl Grignard reagents react with $SiCl_4$, and $(CF_3)_2SiCl_2$ has been isolated. It may also be possible to prepare polymeric compounds of the type $-Si(CF_3)_2-O-Si(CF_3)-O-$ by reaction of perfluoro iodides and Si–Cu.

The paper contains a list of infra-red wavelengths characteristic of functional groups in fluorine compounds, compared with values for corresponding hydrocarbons. (*See* also Abs. 1260—1951.)
H. C. E.

759. Transfer of hydrogen in organic systems. R. P. Linstead, E. A. Braude, P. W. D. Mitchell, K. R. H. Woolridge, and L. M. Jackson. *Nature*, 1952, **169**, 100–3.—The term " hydrogen transfer " is used to include both intra- and inter-molecular reactions of organic compounds in which covalently bonded hydrogen atoms change their site of attachment. It is discussed under three headings :

1. *Catalysed disproportionation.* An example of this group is the reaction of *cyclo*hexene at room temp with Pd-black as catalyst :



. . . . . (1)

Other compounds undergoing the reaction are *cyclo*hexadienes and dihydronaphthalenes. It has been shown that *cyclo*hexadiene is not an intermediate in reaction (1), and it follows that removal of all four H atoms probably occurs simultaneously.

2. *Catalysed hydrogen transfer to foreign acceptors.* Hydrogen transfer also takes place below 100° C with Pd-black as catalyst between *cyclo*hexene and compounds such as octene, stilbene, and unsaturated aliphatic acids to give the corresponding saturated compounds; and between *cyclo*hexene and nitro compounds, which are reduced to the corresponding amine. Transfer does not occur between *cyclo*hexene and aldehydic, keto, carboxylic, or cyano groups.

Transfer and disproportionation occur simultaneously, and with many "unlike" acceptors transfer predominates, although it proceeds more slowly than does disproportionation when the acceptor is absent. Other hydro-aromatic compounds, and hydro-heterocyclic compounds, can act as donors, but the relative effectiveness of different donors depends upon the acceptor.

3. *Uncatalysed transfers.* Quinones undergo reactions of the type: benzoquinone + 1 : 4-dihydronaphthalene → hydroquinone + naphthalene. When side reactions are excluded hydrogen transfer is quantitative and exhibits second-order kinetics. The rates of reaction of a number of related quinones are in linear relation to their oxidation-reduction potentials. H. C. E.

760. Adsorption of aromatic hydrocarbons in nonaromatic media on carbon black. M. van der Waarden. *J. Coll. Sci.*, 1951, **6**, 443–9.—The following hydrocarbons, in *n*-heptane or white mineral oil solution, were adsorbed at room temp on carbon black of measured surface area: benzene, naphthalene, anthracene, phenanthrene, xylene, and alkylated naphthalenes containing (*a*) one C_8 alkyl chain, (*b*) one C_{16} and one C_{12} chain, (*c*) 2–3 C_{14} chains. Adsorption isotherms are given.

Calculation of the surface areas of the adsorbed compounds indicates that aromatic nuclei are adsorbed flat on the carbon surface and the alkyl chains remain mobile in the liquid. These alkyl chains appear to be mutually repulsive. H. C. E.

Analysis and Testing

761. Determination of SO_2 and SO_3 in flue gases. P. F. Corbett. *J. Inst. Fuel*, Nov. 1951, **24** (140), 247.—An analytical method for the determination of small quantities of SO_3 in the presence of excess SO_2 is reviewed. The method consists of the absorption of SO_3 in *iso*propyl alcohol together with a little of the SO_2 and the absorption of the remainder of the SO_2 in a suitable oxidizing agent such as a standard solution of iodine or hydrogen peroxide. The estimation of the SO_3 in the inhibited solution is based on the turbidity produced by the precipitation of barium sulphate. A photo-electric cell measures the obscuration of light produced by the precipitate, and the percentage obscuration is then related to the SO_3 content of the original solution. It was found necessary to control working conditions rigidly to obtain an accurate result. An apparatus is described which was designed to sample flue gases from a boiler and estimate SO_2 and SO_3 concentration leaving the equilibrium existing between the oxides undisturbed. Some results obtained are given, and they show that the range of SO_3 measured is such as would be expected from dew-point observation on similar plant. Relationship between SO_3 concentration and dew-point is discussed. Fifteen literature references. D. K.

762. Vibrating plate viscometer. J. G. Woodward. *J. Coll. Sci.*, 1951, **6**, 481–91.—The construction and operation of the viscometer are described. In principle a thin circular plate of thickness 0·01 inches is made to vibrate in its own plane in the liquid the visc of which is to be determined. The damping effect is dependent on the product of coeff of viscosity η and density d of the liquid, and is measured by the amplitude of vibration of a reed attached to the plate. The vibration is measured by means of piezo-electric barium titanate blocks, and the voltage E thus generated is related to the visc by the equation $\eta d = k(1/E - 1)^2$, where k is a constant.

The instrument has the following advantages: (*a*) measurements can be made in the range 10^{-1} to 10^5 cp; (*b*) measurements are made within a few sec, and the instrument can be modified for continuous recording; (*c*) samples of vol 0·5 ml can be used at temps from 100° C downwards. The apparatus can be used for Newtonian and non-Newtonian fluids, and its accuracy is of the order ±5%. H. C. E.

763. Measurement of viscosity under pressure. Anon. *Petroleum*, Feb. 1952, **15** (2), 39.—An abstract of Rept No. 17, Sponsored Research (Germany), which describes the measurement of the visc of lubricating oils under pressures up to 2000 atm carried out by Dr E. Kuss on oil samples supplied by DSIR.

Densities were determined using a piezometer partly filled with mercury, and visc by two methods. One apparatus was designed on the ball-drop principle, the second was a capillary method which permitted the examination of both liquids and gases

under pressure without opening or rotation of the apparatus. From the results of measurements on fifty oils the possibilities of mathematical representation were studied. R. E. P.

764. Burning velocities—acetylene and dideutero-acetylene in air. R. Freidman and E. Burke. *Industr. Engng Chem.*, 1951, **43** (12), 2772–6.—The apparatus and experimental procedure are described for determining flame speeds of C_2H_2–air and C_2D_2–air mixtures. Results showed that the C_2H_2–air mixtures gave rise to higher flame speeds than the C_2D_2–air mixtures. A mechanism is put forward to account for this. E. J. C.

765. Spectrochemical research in petroleum industry. J. J. Glogoczowski. *Nafta*, Jan. 1951, **7**, 2–8.—History and basic principles of absorption and emission spectroscopy and their use in analysis of soils, cores, fuels, and lubricants. Further dealt with is mass spectroscopy, which is useful for identifying hydrocarbon radicals. To avoid confusion between radicals of the same $\frac{M}{e}$ value, *e.g.*, CH_3^+ and OH^+ different ionizing potential must be used in each case. M. S.

766. I.F.P. equipment for hydrocarbon detection. E. Vellinger, C. Labbe, and R. Monicard. *Rev. Inst. franç. Pétrole*, 1951, **6**, 403–12.—In conjunction with I.F.P. hydrocarbon detector No. 3 (cf. Abs. 2755—1950) auxiliary equipment has been designed for the degassing of drilling muds, cores, and cuttings. Degassing is done either by vac or heat, latter is used in an apparatus adapted for automatic operation. Operational details are described and diagrams given. Hydrocarbon detector previously described has now been adapted for continuous automatic operation; flow and circuit diagrams are shown. Entire degassing and measuring equipment can be installed in a mobile trailer laboratory for field use. V. B.

767. CFR test engine calibrator is time saver. J. V. Mark. *Petrol. Process.*, 1951, **6** (12), 1403.—A device is described for setting the volume clearance of a CFR test engine. Constructional details are given. D. W. F.

768. Swiss standards. Sulphur content of mineral oils. *Schweiz. Arch. Ang. Wiss. Tech.*, 1951, **17**, 381–2.—Draft. Quartz-tube method akin to IP 63/51 (T) is prescribed, but S is determined gravimetrically as $BaSO_4$. Repeatability and reproducibility limits are $\pm 0{\cdot}01 + 0{\cdot}02$ A and $\pm 0{\cdot}01 + 0{\cdot}04$ A respectively. V. B.

769. German standard DIN 51757. *Erdöl u. Kohle*, 1951, **4**, 796.—Error is notified in draft standard (*see* Abs. No. 2710—1951), figures for $d_{15/4}$ and $d_{20/4}$ having been transposed. V. B.

Crude Oil

770. Sulphur compounds in crude oil and its products. Glaser and Zielinski. *Proc. of Main Petroleum Institute*, (Polish) *Ministry of Mining*, Katowice, 1951, **No. 6**, pp. 20.—A review of known properties of sulphur and its compounds in so far as they affect oil products. A list and brief descriptions of many sweetening processes is given, followed by description of experimental results of counter current extraction using NaOH aq. and CH_3OH, proving that there is an optimum rate of flow giving maximum extraction. M. S.

Engine Fuels

771. Hydrocarbons in the diesel boiling range. R. W. Hurn and H. M. Smith. *Industr. Engng Chem.*, 1951, **43** (12), 2788–93.—Data are presented on the ignition characteristics of three diesel fuels, which were separated into paraffin–naphthene and aromatic cuts, at 525 p.s.i. bomb pressure, and between 850° and 1050° F.

Pure hydrocarbons were also tested, and in all cases ignition lag decreased with increase in number of carbon atoms at 300 p.s.i. bomb pressure and between the range

850° to 1050° F. Hydrocarbons tested were: paraffins—heptane to octadecane; olefins—1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene; naphthenes—methyl*cyclo*hexane, ethyl*cyclo*hexane, butyl*cyclo*hexane, di*cyclo*hexane, and decalin. In general, ignition quality decreased with unsaturation. E. J. C.

772. Burning bunker oils in American diesel engines. E. B. Rawlins, E. D. Newell, and D. C. Macmillan. *Motor Ship*, Dec. 1951, **32** (381), 338.—The paper bases its findings and recommendations on several land installations, with modern American engines in the moderate speed range suitable for geared or electric drive. An installation of 13,500 normal s.h.p. was selected as representing a practical marine-diesel installation. Five engines are used for propulsion, with three smaller units providing auxiliary power. The fuel system for such an installation, the arrangement of equipment on engines using the controlled pressure fuel system, and using individual injection pumps are all shown schematically. The equipment and method for processing the fuel should be no different for a marine than for a stationary installation. The success of a diesel engine operating on bunker oils depends primarily upon the preparation of the fuel, and recommendations for the proper cleaning and heating of the fuel are made, as well as for the sizing of the processing equipment. Care of the lubricating oil is also important, and, because of the nature of contamination from heavy fuels, experience indicates the need for centrifuging as well as filtering the oil. Economic considerations and operating costs are illustrated graphically and by tables. Based on June 1951 prices the saving in the fuel bill of a motor ship burning bunker oil instead of marine diesel oil will be about 35% for East Coast of America ports. With properly prepared bunker fuel and proper operation, engine wear rates are no greater, if as great, as when using diesel oil. U. M.

773. Initiation of detonation in gases. G. B. Kistiakowsky. *Industr. Engng Chem.*, 1951, **43** (12), 2794–7.—A review of published theories and facts on the mechanism of initiation of detonation by flames. Comments are included on non-stationary detonation waves. Twenty-six references. E. J. C.

774. Auto-ignition by rapid compression. J. C. Livengood and W. A. Leavy. *Industr. Engng Chem.*, 1951, **43** (12), 2797–805.—The rapid compression technique provides a convenient means of recording pressure–time and inflammation characteristics of auto-igniting mixtures which react too rapidly for study in a conventional bomb.

Auto-ignition of homogeneous fuel–air mixtures may occur in a variety of ways, both with regard to the pressure–time history and the manner in which the inflammation develops. Motion pictures show that the inflammation does not generally occur uniformly throughout the mixture. The reason for this non-uniformity is not definitely established, but schlieren photographs reveal numerous localized temp gradients which appear in the mixture. These gradients can be explained on a physical basis.

In the light of evidence presented, a re-examination of the meaning of such familiar terms as "delay," "explosion," and "flame front" seems to be called for. As a start in this direction a rigorous definition of delay is given. This definition permits the establishment of a criterion for appraising the advantages and limitations of bombs, rapid compression machines, and shock tubes as apparatus for investigating auto-ignition phenomena. (Authors' abstract.) E. J. C.

775. Two stage auto-ignition of some hydrocarbons. W. J. Levendahl and F. L. Howard. *Industr. Engng Chem.*, 1951, **43** (12), 2805–14.—An apparatus and experimental procedure are described to investigate the causes of combustion knock. Seventeen different hydrocarbons and oxygenated compounds were tested, and it was found that two distinct stages occurred during auto-ignition. The first of these was characterized by the emission of light of low intensity and a moderate pressure generation, while in the second stage, light of high intensity was emitted with a sharp rise of pressure.

Fuel structure greatly influenced the pressure required to initiate the first stage, its duration, and heat liberated in it. It was concluded that the occurrence of detonation during the second stage was determined by the first-stage reaction. E. J. C.

Gas Oil and Fuel Oil

776. Swiss Standards. Mineral fuel oils. *Schweiz. Arch. Ang. Wiss. Tech.*, 1951, **17**, 380.—Draft (2nd revision) standard 81160 covering high-speed diesel fuel, special fuel oil, light fuel oil, and industrial fuels grades III, IV, and V. Following are major requirements: visc (max, cs) (at 20° C for three lightest fuels) 9, 9, 15 (at 50° C for industrial fuels) 35, 60, 150; fl. pt. (closed) 65° C min on all grades; S (%) 1·0, 1·0, 1·5, 3·0, 3·5, 4·0 max. Diesel grade calls for D.I. min 50, on this and on special fuel min % vol at 360° C is 90 and max cloud −6° C. For three lighter fuels sum of C_6H_6 insol + H_2O is 0·1, 0·1, 0·2% max, on three industrial grades max sediment and water are 0·25 and 0·5% respectively. V. B.

777. Petroleum-derived fuels in the U.S.A. Fortain. *Bull. Ass. franç. Tech. Pétrole*, 1951 (90), 25–33.—Lecture. Review of U.S. position, based on 1948 figures and with special reference to comparison with France. In coal units total *per capita* consumption in U.S. is 3·6 times greater than in France, whilst for space heating it is 5 times greater, 40% of U.S. liquid fuels being used for this purpose. Pet provides 39% of U.S. energy requirements, but only 6% in France. Types of fuel oils used in both countries are briefly considered, and distribution of total fuel consumption between railways, electricity generation, industrial use, and space heating is shown in tables. V. B.

Lubricants

778. Oil engine cylinder-lubrication problems. Anon. *Motor Ship*, Oct. 1951, **32** (379), 286.—Short extracts from a paper by J. J. Broeze read at the World Petroleum Congress. Main problems met with in marine engines, particularly of two-stroke type, are cyl and piston-ring wear when running at high output, and isolated cases of corrosion of parts in the crankcases due mostly to presence of combination of sulphuric acid from used cylinder oil and salt. A correlation is suggested between cylinder and piston-ring wear and fuel sulphur content, but the two-stroke power cycle itself is likely to give rise to conditions which promote "scuffing." The four-stroke engine is less vulnerable to this type of wear, and so successful attempts to burn heavy fuels, which also have relatively high sulphur contents, have been made mostly on four-stroke engines. The oil engine is not sensitive to the small amounts of organically bound ash in many residual fuels, and with proper purification of the fuel would be able to work with a wide range of fuels. Sulphur in the fuel, more than any other factor, is responsible not only for abnormal wear but also for most of the fouling typical of the high-speed oil engine. Reduction of the sulphur content of heavy distillates has not been possible, but the production of additive-type oils has minimized its effect, and it appears that the practical difficulties due to sulphur may be solved in an economical fashion by these additives. U. M.

779. Phase behaviour of lubricating greases. T. D. Smith. *Petroleum*, Jan. 1952, **15** (1), 5–8.—Commercial greases are usually extremely complex systems, and are generally not in thermodynamic equilibrium. However, by comparing the behaviour of greases with simple binary or ternary systems it may be possible to deduce certain ideas concerning the phase nature of the more complex systems. Phase diagrams represent the solubility relations of soap in oil, and can be used to give some idea of the temp required to prepare a satisfactory dispersion of soap, and to indicate the range over which a grease will maintain a required texture.

Some of the methods employed in phase studies and some of the results which have been obtained are reviewed. R. E. P.

780. Lubrication-bearing problems in aircraft gas turbines. E. M. Phillips. *Mech. Engng*, 1951, **73** (12), 983.—Experience has confirmed that for aircraft gas turbines, ball and roller bearings are most suitable, due to low power loss, low starting torque, and provision for angular movement during manœuvres. Difficulties in separating oil from air and in the handling of large volumes of oil mist have caused oil-mist lubrication to be superseded by solid oil-jet systems. Oil is metered to the bearings, some of the oil acts as a lubricant, and the remainder cools the bearings. At temp

below −30° F troubles were encountered using a grade 1010 lubricating oil, and a grade 1005 petroleum oil was developed which gave satisfactory performance at temp down to −65° F. On re-starting turbines after shut-down, seizure of bearings occurred before adequate lubrication was attained. Replacement of the brass cages by silver-plated cages showed great improvement, and more recent tests indicate that cages of H Monel are even more suitable. The author suggests that ball races should not be located where the lubricants can evaporate on shut-down, unless lubrication can be provided prior to re-starting. T. T.

Bitumen, Asphalt, and Tar

781. Influences of physical properties of oily preservatives on the penetration into wood. W. Liese. *Bitumen, Teere, Asphalte, Peche*, 1951, **11** (2), 276–9.—The following investigations are intended to explain further the cause of the varying behaviour of oils by extending the work of previous investigators on the dependence of pen on visc and surface tension to include the influence of sp. gr. Forty-one commercial materials embracing a wide range of surface-tension visc and sp. gr. were used. Experimental procedure is described for the following observations: ht of rise and spread of a wood preservative on filter-paper; spread on glass and wood surfaces; pen capacity, rate, and depth. From the tabulated results no correlation appears to exist between the rise of an oil on filter-paper, or between the spread on a glass or wood surface and the pen capacity into wood. In the first place visc, in the second place surface tension, is significant for the spread of a wood-preservative oil on the surface and for the pen rate. Depth of pen of a wood-preservative oil is influenced by physical properties, visc, surface tension, and sp. gr., but purely chem factors often exert a major influence. Fourteen literature references. R. T.

782. Essential knowledge about German natural asphalt mastic. O. Martin. *Bitumen, Teere, Asphalte, Peche*, 1951, **11** (2), 285–8.—A brief review of the use of asphalt mastic in the early times from 4000 B.C., with illustrations of coast protection on the Tigris and the sealing of a Babylonian bathroom. The art appears to have been forgotten until the discovery of Val de Travers natural asphalt in Switzerland in 1712 opened up a new era. A description, with illustrations, is given of the asphalt works at Vorwohler in Germany, where different grades of mastic are produced from natural asphalt rock. The extensive application of asphalt mastic for roof coverings, water sealing, and for floors in power-stations, transformer rooms, and where explosives are produced is discussed. R. T.

783. Bitumen insulators and their use for concrete protection. O. Lissner. *Bitumen, Teere, Asphalte, Peche*, 1951, **11** (2), 271–6.—Economical considerations favour the use of bitumen products for concrete protection, but coal tar—chiefly aromatic—is not so stable to chemicals as the predominantly aliphatic pet bitumen. The properties of tars may be improved by boiling with binding agents containing Cl_2 at 180° to 220° C. Such compounds, chlorinated rubber, chlorinated buna, etc., convert normally liq tar products into hard, ductile materials resembling the higher-melting aliphatic bitumen types. Conventional physical and chem methods for the rapid identification of bitumen–tar mixtures are given. Bitumens may be applied hot as adhesives and for filling joints, or cold as emulsions with water or solutions in organic solvents. Great care is necessary in the choice of a bitumen for a sp purpose, and its application, particularly in confined spaces, must be governed by official regulations. Resistance of coatings not only to water but to dil and conc acids, alkalis, and salt solutions is confirmed. The assumption for successful resistance to attack is freedom from porosity, imperviousness, and good adhesion. The concrete surface must be smooth and the insulating materials homogeneous. The coating must be at least 50 μ, for this two coats are applied, a third if necessary. A testing method for freedom from porosity is described and illustrated. R. T.

784. Contribution to the study of Limagne bitumens. M. Louis and F. Bienner. *Rev. Inst. franç. Pétrole*, 1951, **6**, 413–20.—Six samples from various bitumen sources in the Limagne area (central France) were investigated. Bitumen content ($CHCl_3$ extraction) was 3·6 to 100% and was analysed for asphaltenes (19·7 to 46·7%), oils (5·6 to 38·1%),

resins (7·7 to 62·6%), sap. val. (28 to 195), S (9·5 to 11·2%, on two samples only). The oils (mol. wt. 446 to 527) were themselves examined for S (6·8 to 10·8%), C, H, O + N (0·9 to 5·7%); C/H ratio was 7·03 to 7·55. Most extensive examination was of bitumen (3·6% yield) from sandstone in Clermont–Ferrand region. After $CHCl_3$ extraction sandstone still retained about 2% org matter, present in two forms (analyses given). Retorting of $CHCl_3$-extracted sandstone yielded 27·3% (on org matter) of oil, which was analysed. It is considered that the $CHCl_3$-insol org matter is a parent substance of pet. V. B.

Coal, Shale, and Peat

785. Contributions to the low-temperature carbonization of coal. G. Lorenzen. *Brennstoff-Chem.*, 1951, **32** (21–22), 324–31.—Comparison with high-temp coking and hydrogenation shows that low-temp carbonization is economical for producing liq hydrocarbons and coke. It is particularly valuable in countries where liq hydrocarbons are absent or insufficient, and suitable coals are available. The hydrocarbons produced are non-aromatic, chiefly fuels, and phenols, a valuable source of synthetic materials. However, the process must be directed towards the production of coke as a main product. In England high-temp coking is directed largely to the production of gas and high-quality smokeless domestic coke. This coke output is supplemented by the low-temp-carbonization plant. Tar is relegated to the background. In Germany tar supplies the real motive for low-temp carbonization. Practice has turned progressively from coking to non-coking fine coal in nut or briquette form, and furnaces have been developed to process all types. The relative merits and efficiencies of the Otto stone furnace and the BT (Brennstoff-Technik) iron furnace are discussed with the aid of numerous drawings. It is indicated that installations can produce coke as the main product with a satisfactory tar yield. R. T.

786. Experiences with the Koppers rotary gas process. F. Bieger. *Brennstoff-Chem.*, 1951, **32** (21–22), 331–9.—A brief description is given of the plant developed and constructed, without a pilot plant, by Koppers for the production of synthesis gas by the gas rotary process from brown-coal briquettes. With minor alterations the plant, as illustrated by a flow diagram, proved satisfactory. Considerable fluctuations in output which occurred during the operation were attributed to variations in the quality of the briquettes due to excessive water cont. Collaboration with the producers resulted in briquettes of improved quality. Theoretical and practical considerations based on experience on the plant and empirically accumulated experience, particularly regarding the residual gas addition and structural improvements on the gasifier, were utilized to attain the necessary improvement of the installation. With the improved plant the output guaranteed by Koppers was exceeded in continuous operation by 65% and at the peak by 90%. Numerous flow diagrams and sectional drawings of the gasifier are presented. R. T.

Miscellaneous Products

787. Chemical products containing fluorine (2). A. K. Barbour and L. J. Belf. *Chem. Prod.*, Dec. 1951, **14** (12), 430–6.—This, the second and concluding part of an article on fluorine compounds, deals first with the synthesis of trifluoro-acetic acid, and then describes the syntheses from " Freons " of the polymers, " Kel F " (polyperfluorovinyl chloride), and " Teflon " (polytetrafluoroethylene), together with their properties and applications. The fluorine compounds next considered are those used as catalysts, namely, anhydrous hydrogen fluoride and boron trifluoride; the methods of preparing these and their properties are outlined. Examples are given of the reactions in which they are employed as catalysts, *e.g.*, alkylation reactions. The article concludes by reviewing some miscellaneous applications of fluorine-containing products, *e.g.*, insecticides and dyestuffs. M. C. B.

788. Relative toxicity of insecticides. S. W. Simmons and W. J. Hayes. *Soap Sanitary Chem.*, Dec. 1951, **27** (12), 148.—This article summarizes health statistics, with particular attention to death or accident using household chemicals, particularly

pest controllers. With rodenticides, sodium monofluoroacetate (1080) has the largest number of fatal accidents, while ANTU has a very good record. Among the newer insecticides, most fatal accidents have been given by organic phosphorous compounds; specific cases are quoted for parathion and tetraethylpyrophosphate. A number of deaths have been attributed to D.D.T. intoxication. The newer compounds on the whole, however, have a good safety record, but the need is stressed for proper care in labelling and public education with these products. N. W. G.

789. Oil fractions as weedkillers. G. E. Barnsley. *Petroleum*, Feb. 1952, **15** (2), 35–6, 55. (*Presented to Assoc. of British Insecticide Manufacturers.*)—The employment of petroleum-oil fractions as weed-killers is discussed. The phytotoxicity of an oil depends on its penetration into the plant and on its inherent phytotoxic properties. Ideally a base oil for weed-killers should have a high aromatic content and should not be too viscous, otherwise leaf penetration will be inadequate. The selective phytotoxicity of an oil fraction is dependent, however, on the ratio between aromatic and non-aromatic parts of the oil and not on the amount of aromatics deposited per unit area. Two types of mineral oils are commonly used for selective weed-killing, mainly power kerosine and white spirits. Tractor vaporizing oil has also been used as well as commonly available oils of low toxicity fortified with such chemicals as DNC and PCP. R. E. P.

790. Significance of hydrocarbon chemistry in the synthetic detergent industry. H. Stüpel. *Erdöl u. Kohle*, 1951, **4**, 687–92.—Synthetic detergents have encroached greatly on the consumption of soap products over the last three years. Apart from freeing more fats for nutritional purposes and widening the detergents market, synthetic detergents have many advantages over carboxylic alkali soaps, such as activity at low concn and at any pH range; neutral reaction; increased wetting powers, emulsification, and dispersion. The fundamentals of the synthesis consist of the combination of a hydrophobic (hydrocarbon) group with a hydrophilic group (usually sulphate or sulphonate). This can be carried out in a number of different ways, the following being those most significant industrially: (1) introduction of hydrophilic group to alkanes by sulphochlorination or sulphoxidation ($SO_2 + Cl_2$ or O_2) yielding alkyl-sulphonates; (2) alkylation of benzene (either by Friedel–Crafts or via the alkane), followed by sulphonation with H_2SO_4, yielding alkyl-aryl-sulphonates; (3) sulphating of higher-mol alkenes, yielding secondary alkyl-sulphates. Recent patents and developments in Europe and the U.S.A. are reviewed. Details of operating conditions and plant flow-sheets are given for a number of industrial processes. Importance is stressed of pet base and synthetic hydrocarbons as raw materials in this fast-expanding industry. Seventeen references. P. V.

791. Surfactant performance. H. L. Sanders. *Soap Sanitary Chem.*, Dec. 1951, **27** (12), 39.—Synthetic surface-active agents were introduced about twenty years ago, and there are now about 1000 brands on the U.S. market. The need for tabulated data to relate performance to chemical type is discussed. Tables of typical values for well-known commercial products are assembled from the literature and author's work covering the following items: cotton detergency (built and unbuilt formulæ); foaming power; wetting properties; surface tension; interfacial tension; spreading coefficient. HLB value (hydrophile–lipophile balance); lime-soap dispersing power; viscs; corrosiveness, and oral toxicity. N. W. G.

792. Cleansers and dermatitis. L. Schwartz. *Soap Sanitary Chem.*, Dec. 1951, **27** (12), 43.—There is some evidence that hand eczema has been increasing in recent years among housewives. The physiology of the skin and sweat glands and the action of dermatitis-producing compounds are discussed. For soap, some people are sensitive to alkali, which swells and removes the keratin layer, also, tendering is given by removal of oils, fats, and waxes from the skin by emulsification. The action varies for different fatty oils used in the soap with different builders, and individuals show considerable variation in their allergies. Synthetics have one advantage in that alkali-sensitive subjects can use neutral detergents, but no general statement can be made because of the wide range of anionics, cationics, non-ionics, and sulphonated

vegetable oils used in detergents. In general, the greater the wetting and emulsifying properties of the product, the more defatting action will be given, with greater liability for sensitive subjects to develop skin troubles. N. W. G.

793. Potash liquid soap solutions. N. V. Feldpush and L. L. Sutker. *Soap Sanitary Chem.*, Dec. 1951, **27** (12), 48.—One effect of the synthetics on the soap industry has been to make available products with a guaranteed specification. The possibilities are discussed of controlling two properties—clarity and viscosity—for 20% liquid potash soaps. The approach was to add comparitively pure fatty acids. It was found: (*a*) saturateds, such as palmitic and stearic acids, gave lower clear point and lower visc in an optimum range of 5 to 10% additions; (*b*) unsaturateds, such as oleic and linoleic acids, gave a lower clear point with no change of visc for 10% additions; (*c*) up to 4% unsaponifiables also lowers the clear point without interfering with the commercial properties of the soap. N. W. G.

794. Sequestering agents in soap. H. van Sluis. *Soap Sanitary Chem.*, Dec. 1951, **27** (12), 91.—Summary of an article from *The Alchemist* 1951, **5** (10), 281, which deals with organic sequestering agents, such as polyamino carboxyl acids and their salts, and nitrilo-triacetic acid. The most important product is ethylenediamine tetracetic acid. These are used in neutral or alkaline solution to de-ionize bivalent or trivalent cations, such as Fe, Al, Cr, and particularly Ca and Mg, acting by the isolation of the metal ion in a non-ionic chelate. These products are applied for water softening in fat, food, and soap industries, and are also useful as anti-oxidants for fats. N. W. G.

795. Sweeping compounds. M. A. Lesser. *Soap Sanitary Chem.*, Dec. 1951, **27** (12), 144.—In addition to collecting dirt without raising a dust, these products assist in reducing the number of airborne bacteria. Apart from simple compounds such as damp sawdust, tea-leaves, etc., these products are of two types: (1) Oil-prepared type for use on wood, steel, terrazzo, etc. U.S. Federal Specifications require volatiles at 110° C 12% max, mineral oil 15 to 20%, clean sand 35 to 50%, wt, sawdust not less than 18%. In formulations, other products such as bran, vegetable meal, salt, as well as perfumes and colouring matter are used. (2) Wax types for linoleum, rubber, asphalt, tile, or mastic floors. These overcome the action of the oil on the floor, by using the wax as a part or whole replacement of the oil. Similar wax ingredients to floor polishes are used, but usually the sweeping compound does not contribute to floor polishing. The presence of sand in all formulæ is to give a product with a suitable particle size and density to be easily swept. The oil or wax emulsion is the wetting agent to make the sweeping compound hold together in use. N. W. G.

796. Recent advances in the manufacture of synthetic rubbers. R. Buret. *Chim. et Ind.*, 1951, **66**, 799–805.—Lecture, reviewing progress since 1948. Advances have been mainly in the field of polymerization and aids thereto, *e.g.*, di-*iso*propyl xanthate introduced in Germany. Factors influencing polymerization are considered under the following heads: temp; cat (*e.g.*, tetrahydrofurane peroxides); emulsifier; ratio of feed vol to emulsion vol (optimum about 2); copolymers; polymerization aids (activators, regulators, etc.); electrolytes; pH. Procedure for cold (4° C) polymerization is discussed, and a typical formulation for this is given. French rubber consumption is 120,000 ton/year, and plans have been made for synthetic production of somewhat less than half this quantity. Doubt is expressed whether capital investment necessary for such plant could be accomplished, and an initial annual capacity of 4000 tons is considered more realistic. V. B.

797. Pigment dyestuffs and litho inks—The significance of pH measurement. J. Keaton. *J. Oil Col. Chem. Assoc.*, Dec. 1951, **34** (378), 586.—The lithographic printing process is briefly described. Water is an active agent in this process, and it has been found that sometimes it will " break through " an offset litho ink during the printing. Investigations into the problem suggest that the pH of the aqueous extract of the pigment is an important factor. A table of pH values of water extracts of various pigments shows different batches of the same pigment from the same source to be very consistent in pH of extract, but indicates that wide variation is possible with different

pigments. From practical observations and on theoretical grounds it is expected that a pigment with a high pH extract is more liable to emulsification than one with a lower pH. Results of comparative tests carried out are in agreement with this belief.
D. K.

798. Pigment surface. H. Mills. *J. Oil Col. Chem. Assoc.*, Nov. 1951, **34** (377), 497.—Relative contributions to paint rheology of various factors, *e.g.*, particle size and distribution, particle shape, extent of surface, and the nature of the surface are discussed. The preparation of lithopone pigmentary particles is described, and a transition point in surface area and internal structure is correlated with rheological behaviour. Ease and completeness of dispersion of the pigment is one of the most important factors in paint-making. Oleo-resinous and oil-water emulsion paints are systems in which a pronounced surface activity of the pigment is very valuable because it offers the following advantages: stability of the system, lower pigment/medium ratio for the same film mattness, better application and film appearance, and improved dry hiding. Surface activity is controlled by the manufacturing heating process, and determines the degree of reversibility of the rheology of the pigment-medium systems. Oil absorption bears a relationship to consistency, and this is discussed in some detail. Many graphs and tables are included. There are ten literature references. D. K.

799. Influence of pigments on the mechanical properties of paint films. H. W. Talen. *J. Oil Col. Chem. Assoc.*, Oct. 1951, **34** (376), 455.—The importance of making tensile tests with unsupported detached films is considered. The dynamometer used in experiments discussed is described. The following mechanical properties were investigated: tensile strength, the modulus of rigidity at 5% elongation, and the elongation at break of unsupported paint films. Paint films with a linseed-oil base containing red lead, iron oxide, and lead oxide as pigments were investigated. Three types of red lead with varying quantities of PbO, paints with iron oxide, and lead oxide mixtures with the same total pigment volume as with the red-lead paints and same PbO contents, and paints with just iron oxide as pigment, were examined.

Results with red-lead paints showed an increase in tensile strength and a decrease in elongation at break point with time. Iron oxide paints showed a decrease in tensile strength and an increase in elongation at break. Paints containing a mixture of these showed intermediate behaviour on ageing proportionate with the iron oxide and lead oxide present in the pigment.

Investigations were also made into the influence of various white pigments, *e.g.*, zinc oxide, lead titinate, titanium dioxide (anatase and rutile types), and other titanium oxide types, on the properties of paint films with an alkyd or a stand oil medium. Different pigments in the same volume proportions showed varying influences on mechanical properties of the paints. Alkyd paints examined had a higher tensile strength than corresponding stand oil paints. In a stand oil medium the differences between the paints are less striking than in an alkyd medium. The literature dealing with the influence of pigments on the mechanical properties of paint films is reviewed.
D. K.

800. The measurement and interpretation of oil absorption. G. E. Bessey and K. A. Lammiman. *J. Oil Col. Chem. Assoc.*, Nov. 1951, **34** (377), 519.—A brief review of the history of oil-absorption measurement is presented. Bulk density measurements of powders and powder–oil mixes are discussed. The true oil absorption of a powder is shown to be the min proportion of oil which will give, with adequate mixing, a mixture with no voids; for a given sample it is a unique value independent of the observer.

Methods described give a definite value, but the direct method is impracticable owing to the length of time required for complete mixing. An indirect method has been developed in which a small known quantity of oil is mixed with the powder, a weighed portion thoroughly compacted under defined conditions, its volume measured, and the density and void content calculated. The amount of oil required to fill the voids obtained from this figure, together with the oil already present practically equals the true oil absorption. Measurements with dry powders tend to give void contents slightly higher than the true value because of difficulty in compacting the dry powder so closely.

The intrinsic properties of a powder which determine its oil absorption are particle-

size distribution, average particle size, and particle shape; the surface area is related as a function of these properties.

True oil-absorption values are independent of the medium provided there is no significant chemical reaction, but time of mixing is dependent on wetting and dispersing properties of the medium.

There are twenty-six literature references. D. K.

801. Fungicides in paints and other protective coatings. W. H. Ritchie. *Paint Technol.*, Nov. 1951, **16** (191), 481.—The utilization of raw materials which are non-nutrients for fungi is recommended wherever possible in the manufacture of fungus-resisting protective coatings. This alone is not sufficient protection where the fungus problem is severe, and the addition of fungicides to the paint would be advisable. Chemicals to be used as fungicides should have, as well as high fungicidal efficiency, no effect on the drying time of the paint or on the film characteristics, good durability, and low toxicity to human beings. A combination of slight water solubility and vapour pressure may be advantageous because it allows the agent to be active at all times. A list is given of chemicals which have been used as fungicides. The preservation of water paints may be effected by mercury compounds or chlorinated phenols. Tests carried out with sodium pentachlorophenate are described. Of the fungicides not highly toxic to humans pentachlorophenol and its sodium salt proved effective for preservation of oil paints. Tests indicate that zinc pentachlorophenate may be an excellent preservative, but shortage of zinc derivatives is a difficulty. For wood preservation both the wood and the paint should be treated with fungicides. Compositions utilizing pentachlorophenol have again proved satisfactory. D. K.

802. Significance of dispersion in colloidal systems. J. Pryce-Jones. *J. Oil Col. Chem. Assoc.*, Nov. 1951, **34** (377), 547.—To determine the degree of dispersion it is necessary to observe the undiluted system, as dilution affects this property.

Dispersion of agglomerates of fine particles is usually produced by shearing. The state of dispersion of a system at rest is determined by the interfacial relationship between the liquid and the surface of the particle. The relationship cannot be expressed quantitatively, but comparative values for different liquids can be obtained. This relationship may be described as " the coefficient of dispersion " of the liquid for the particular species of particle. How the " coefficient of dispersion " of various reagents can be compared by measuring the relative visc of the suspension is illustrated. Also, it is shown how to determine the amounts of added dispersing agents necessary to produce a system wherein the visc is independent of the rate of shear or concentration beyond which the relative visc is constant. D. K.

803. Metal-monolayer interactions. G. A. Wolstenholme and J. H. Schulman. *J. Oil Col. Chem. Assoc.*, Dec. 1951, **34** (387), 571.—The interactions between metal ions and fatty acids have been investigated by measuring the mechanical properties of fatty-acid monolayers on metal-salt solutions at different pH values. Materials used for experimental work were myristic acid, ferric chloride, aluminium sulphate, cupric chloride, cobaltous chloride, manganous chloride, and calcium chloride. Hydrochloric acid or sodium hydroxide was used to adjust pH. Force/area curves were obtained for myristic acid alone and in the presence of various salts at different pH values. When basic metal ions interact with a fatty acid monolayer and the latter is solidified the molecules are immobilized at the surface. It is thought that the molecules are spaced on a basic ion network under the monolayer. When the fatty acid is ionized the monolayer is stable to compression, where it is non-ionized the solid film is weak. The influence of steric factors on the solidification of the monolayer is discussed. Results show that a fatty acid interacts with a metal-salt solution in a well-defined pH range. Similar results were obtained with pigment surfaces. Solubility of a solid surface in water influences adsorption of a fatty acid, for it determines the availability of metal ions at the surface of the solid. D. K.

804. Process control of stand oils during cooling. G. H. Hutchinson. *Paint Mnfr*, Dec. 1951, **21** (12), 437.—Methods of calculating the visc increases which take place during " the cooling down " period of a fast-bodying oil and predicting the " cooling down " visc of a stand oil for a particular final visc are considered. Particular aspects

discussed include : visc control at constant process temp, commercial bodying of stand oils, use of formula, calculation of heating and cooling allowances, cooling allowances for oil processed on plant scale, proof of formula by graphical integration, etc. The Van Mikusch formula is used to calculate cooling equivalents under conditions involving constant rate of cooling. Consideration of rate of cooling, rate of bodying, and doubling interval enables cooling or heating-up allowances to be calculated by the graphical integration method. The rate of bodying of a drying oil is dependent to a large extent on plant conditions as well as temperature. Methods described have not proved satisfactory for wood oil/linseed oil mixtures. D. K.

805. A new aspect of suspension stabilities. G. D. L. Schreiner. *J. Oil Col. Chem. Assoc.*, Dec. 1951, **34** (378), 581.—Work has been carried out to obtain further evidence on the influence of the absorbed layer and to show that the reversibility of adsorption determines the properties of suspensions. Suspensions of copper, nickel, and zinc oxides in various polar and non-polar organic liquids were prepared under controlled conditions. Results are tabulated and photographs presented. Microscopic examination showed that the difference in sedimentation rates is due to the deflocculation of the suspended oxide. Factors affecting these rates are discussed. It seems that in the systems examined an irreversibly adsorbed solvation layer is necessary for the formation of the more stable suspensions. D. K.

806. 400,000 tons of sulphur a year from oil and gas. A. L. Foster. *Petrol. Engr*, 1951, **23** (11), C3–4.—A survey of projected sulphur-recovery units in the U.S. shows that half the million tons world deficit of sulphur may be made up by 1953. Nearly 400,000 tons/year is the estimated output of oil and gas company units, and another 500,000 tons annual capacity is envisaged from deposits in the Mississippi delta area. Within two years an additional 1½ million tons annual capacity should be available, which will be more than required to make up the present deficit. E. K. J.

807. Naphthalene : now and tomorrow. C. J. Baker. *Chem. Engng*, 1951, **58** (11), 375.—The shortage of naphthalene experienced in the U.S.A. due to the increased use of phthalic anhydride is likely to continue for a few years. Sources of naphthalene, improved techniques for recovering it, and substitutes are reviewed. D. H.

Corrosion

808. Corrosion and its control. M. E. Parker. *Oil Gas J.*, 6.12.51, **50** (31), 111 ; 13.12.51, **50** (32), 109 ; 27.12.51, **50** (34), 86.—Pt 38 of this series deals with use of test specimens for corrosion studies, and states fundamental principles regarding their selection. Materials considered more resistant than required, and less resistant, should be used, together with specimens of material already in use. Precautions in cleaning and in mounting the specimens are necessary.

Pt 39 discusses laboratory tests of materials for use in corrosive media. Laboratory tests cannot exactly duplicate service conditions. Thin specimens should be used in corrosion tests, fluid velocities should approximate service conditions, and in addition several velocities above and below should be used.

Final decisions should be made on basis of plant tests.

Pt 40 deals with corrosion tests on operating equipment. Chemical effects are capable of quantitative interpretation ; and a corrosion rate may be found by measuring the loss of an anion such as chloride or sulphate rather than by gain in concentration of a suitable ion.

The current density on metal surface is of major importance. G. A. C.

809. Device aids corrosion study. D. H. Stormont. *Oil Gas J.*, 6.12.51, **50** (31), 92.—The device permits corrosion coupons to be readily introduced or removed from pipelines and similar equipment while in use. It is an adaptation of the " Scotch " nipple which employs a removable gauge-carrier plug through use of special high-pressure lubricator. A sketch of device is provided. G. A. C.

810. H_2S and Co_2 corrosion of carbon steel in natural-gas processing plants. D. E. McFaddin. *Oil Gas J.*, 13.12.51, **50** (32), 97.—Some simplified observations of corrosion

in processing hydrocarbons at the Union Co.'s Santa Maria plant, California, are given, where damage by CO_2 and H_2S has been severe and costly.

Among conclusions listed are that corrosion due to CO_2 is no problem provided no water is present, whilst in presence of free water CO_2 becomes highly corrosive; combination of CO_2 and H_2S plus water is much more corrosive than combinations in which either H_2S or CO_2 is absent. Caution should be applied in use of neutralizing agents.

The several manners by which H_2S and CO_2 attack steel are also listed. G. A. C.

811. Protecting refinery pressure equipment from graphitization. D. B. Rossheim. J. J. Murphy, R. H. Caughey, and W. B. Hoyt. *Petrol. Process.*, 1951, **6** (12), 1385–8. (*From report presented before Ann. Mtg ASME, Atlantic City*, Nov. 25–30.)—The results of a study, made by Kellogg Co. refinery engineers, of graphitization of steel in high-temp equipment are reported. It is based on recent investigations of three integral-clad catalytic reactors, where welded seams had developed cracks after 53,000 hr operation at 900° to 975° F. The section of the report referring to suggestions for protecting existing equipment from the effects of graphitization, and for the selection of steels and other materials for construction and maintenance of new equipment, is presented in full. A further part dealing with the causes of cracking and a theoretical study of stresses in bimetallic construction is summarized. D. W. F.

812. Pigment/vehicle relationship in anti-corrosive paints. J. E. O. Mayne. *J. Oil Col. Chem. Assoc.*, Oct. 1951, **34** (376), 473.—A review is given of the present position regarding the inhibition of corrosion of iron and steel by paints. The theory of corrosion and some general properties of unpigmented paint films are discussed. Pigments used in anti-corrosive paints can be divided into three classes, inert, basic, and soluble.

Unpigmented paint films inhibit corrosion by their high electrolytic resistance, and when immersed in solutions of electrolytes take up a change which restricts their permeability to salts.

Paints prepared with inert pigments should be based on vehicles which are as impermeable as possible to water and salts.

Lead, zinc, barium, calcium, and strontium linoleates render water non-corrosive. Basic pigments form soaps with linseed oil or linseed stand oil. This should be encouraged and controlled by means of a suitable pigment when these pigments are used for protection against atmospheric exposure. In the presence of salt (seawater) the vehicle should be alkali-resistant.

The most important pigments in the soluble class are the metallic chromates. Zinc chromate and zinc tetroxychromate were found to inhibit the corrosive action of water, probably due to soluble chromate ions; when ground in drying oils they may function as basic pigments and form soaps. D. K.

813. Alcohol *vs* construction materials. Anon. *Chem. Engng*, 1951, **58** (11), 288.—Corrosive effects on seventeen materials and coatings are reviewed. D. H.

Engines and Automotive Equipment

814. Wear of fuel injection equipment and filtration of fuel for compression-ignition engines. A. E. W. Austen and B. E. Goodridge. *Gas Oil Pwr*, 1951, **46**, 300–3.—Wear of injection equipment was examined by pumping fuel containing alundum particles of mean dia 32, 12½, 3½, and $<2\ \mu$ at a concentration of 0·03 g/l. The test was continued until 2 g of solid had been passed. Qualitatively, the determining factor causing unsatisfactory performance is wear on the pump plunger and barrel near the helix, and it is lack of balance in delivery from line to line rather than fall-off in delivery which causes rejection. Quantitatively, measurements were made of the mean wear depth and max wear depth around the periphery of barrel and plunger, and these values are given in a table. The max wear depth was 9·0 μ.

Filter tests were made using the alundum/fuel mixtures above, in quantity less than the amount required to form a single layer on the filter. The outflow was passed

through filter-paper, which was subsequently ashed and weighed to measure the amount of solids passed by the filters. Flow by gravity, pulsating, and vibratory flow were examined for fourteen different filter elements. It is concluded that: (1) the life of the filter material should be related to the expected life of the pump elements; (2) the volume of the filter element should be determined by the expected concentration of solids in the fuel; (3) the filter area should be determined by considering the vol of fuel that it is required to filter. H. C. E.

815. Maintenance of internal combustion engines—filtration of air and oil. P. H. Moore. *Petrol. Engr*, 1951, **23** (7), C113–17.—Results are presented of tests carried out on a standardized single-cyl four-stroke diesel engine with air supplied which contains a controlled concentration of silica dust. Repeat experiments were carried out using: (1) a filter on the air intake and (2) filters on both the air and oil flows. The wear of the standard pistons, cyls, rings, valve stems, bearings, and crankshaft journals are shown graphically for the three cases, and the reduction in wear effected by the use of filters is emphasized. E. K. J.

816. Two-stroke diesel gas turbine compounded engine. Anon. *Gas Oil Pwr*, 1951, **46**, 344.—The Napier Nomad is intended as an aircraft engine. It comprises a twelve-cyl horizontally opposed loop-scavenged C.I. engine which delivers power to one half of a counter-rotating propellor. Exhaust gas from the engine is fed into two co-axial gas turbines, of which one drives the other half of the propellor, whilst the other drives an axial compressor used for pressure-charging the C.I. engine. Two auxiliary combustion chambers provide additional power for the take-off.

It is claimed that the design permits high thermal efficiencies, with low fuel consumption over a large range of powers. The engine develops 300 s.h.p. plus 320 lb thrust at take-off, and its fuel consumption at max continuous rating is 0·36 lb/h.p/hr. The dry weight is 4200 lb. H. C. E.

817. Combustion problems of the gas turbine. I. Lubbock. *Gas Oil Pwr*, 1951, **46**, 289–92.—Design of burners and combustion chambers is discussed from the standpoint of combustion efficiency. Oil fuels only are considered, and a table is given of the characteristics of grades suitable for the gas turbine. In general, the oil should be pre-heated, if necessary, so that its visc at the burner is 50 sec Red I (100° F) to ensure fine atomization.

Illustrations are given of various types of burners. It has been shown that, for a simple jet, the mean dia of the droplets increases with the orifice size and decreases with increase in pressure. Hence to cover a wide range of fuel input the duplex burner was designed. Essentially, this comprises a small nozzle within a larger one, the former being used at low rates of flow and the two employed together for high flow rates. Burners with various types of spill return are also available.

Combustion chambers must be so designed that: (1) mixing and combustion occur before the oil spray is chilled; (2) for effective combustion the mixture is aerodynamically stable. The combustion efficiency deteriorates if combustion occurs in the presence of $>100\%$ excess air, and even this amount may be too much for satisfactory working. Two types of combustion chamber are illustrated.

As the rate of combustion is increased it is necessary to increase the turbulence of the mixing air. The pressure drop across the combustion chamber $\propto$ (combustion intensity)$^{1.5}$. For aircraft engines the pressure drop is of the order 2 p.s.i. for a combustion intensity of 3×10^6 B.Th.U/hr/cu.ft/atm. The difficulties involved when a chamber, satisfactory on the test bench at atmospheric pressure, is operated under pressure are mentioned. H. C. E.

818. Trends in British industrial gas turbine design. Anon. *Gas Oil Pwr*, 1951, **46**, 345–7.—Almost all gas turbines now under development are in one of the two groups 750 to 2000 kW and 10,000 to 20,000 kW, and all are intended for electrical-power generation. The components are discussed under the headings: compressors, heat exchangers, combustion chambers, burners, and turbines.

Because the gas turbine can be split into such components that can be developed separately, the tendency hitherto has been to assemble the components loosely and connect by ducting. This procedure led to untidy design and heat losses, and now the

turbines are being designed and built as a whole, with consequent gain of neatness and compactness.

The article concludes with a short discussion of the most urgent problems still unsolved. H. C. E.

819. Allen auxiliary service marine gas turbine. Anon. *Gas Oil Pwr*, 1951, **46**, 265–71.—This set comprises an axial-flow compressor (C.R. 4½ : 1) driven by a two-stage turbine, an annular heat exchanger, multi-chamber combustion system disposed symmetrically around the engine, and a single-stage power turbine driving an Allen alternator. The set was designed to give 1500 b.h.p. with a sp. fuel consumption of 0·745 lb/b.h.p/hr. The various components, which are independently removable, are separately described.

The lub.-oil system comprises two gear-type pumps, one supplying oil at 120 p.s.i. to the governor oil system and the other lubricating the bearings and gearing at 45 p.s.i. The turbine is fitted with Simplex-type burners, and the amount of fuel controlled by a throttle and by the speed governor operating through an oil relay.

In starting, the compressor is run up by electric motor to 1500 r.p.m., and torch igniters between the combustion chambers are lighted by spark. When satisfactory ignition is attained the main fuel supply is switched on. The starting motor continues to assist the turbine up to 2500 r.p.m., and as the turbine approaches no-load speed the governor comes into action. The turbine is normally operated at no-load speed for 5 min before further loading. H. C. E.

820. Gas-turbine plant for a cargo vessel. J. J. McMullen. *Motor Ship*, Dec. 1951, **32** (381), 362.—Discusses a conservative gas-turbine plant for a cargo vessel operating under present-day temp and pressure limitations, and designed for long life. The ship selected is of C-3 type, and the plant proposed is a 8500-b.h.p. installation. Only selected open and closed cycles and only axial-flow compressors are considered. Plant arrangement and operating characteristics are discussed and compared for open and closed cycles, and based on investigations described, the closed cycle is selected as the more practical for this particular use. Disadvantages of the closed-cycle plant are all related to the air heater. Specific cycle operating characteristics are summarized, and machinery arrangement discussed and illustrated. U. M.

821. General service diesel launch. Anon. *Gas Oil Pwr*, 1951, **46**, 332–4.—This launch, intended for fast commercial transport, is capable of a speed of 17 knots. A general description of the accommodation and equipment is given.

The vessel is powered by a Rover Meteorite engine rated at 275 b.h.p. at 2300 r.p.m., the max rating being 320 b.h.p. at 2400 r.p.m. This eight-cyl engine has the cyl, of bore and stroke 5·4 inches and 6 inches respectively, arranged in two banks inclined at 60°, and its C.R. is 16·5 : 1. Ricardo Comet Mark III combustion chambers are fitted, and each cyl carries two inlet and one exhaust valve, which is sodium-filled and tipped with Stellite.

Dry-sump lubrication is employed, and a pump provides lub. oil at high pressure to the main and big-end bearings; the valve mechanism is lubricated at lower pressure. The closed-circuit fresh-water cooling system is thermostatically controlled.

The reverse gearbox has its separate oil sump, pumps, filter, and oil cooler. Electrical starting is achieved by two 24-V axial motors.

The article is illustrated by two cuts and two line drawings. H. C. E.

822. Marshall two-stroke two-cylinder diesel. Anon. *Gas Oil Pwr*, 1951, **46**, 258–60.—This vertical unit has two cylinders of bore 5¼ inches and stroke 6 inches, giving a swept volume of 260 cu. in. It develops 50 b.h.p. at 1250 r.p.m., and the C.R. is 16 : 1. A Roots-type blower, chain-driven from the front of the engine, supplies scavenging air to a rectangular manifold. The C.A.V. pintle-type injector sprays fuel into a thimble-shaped chamber in the cyl-head.

The cooling water is circulated by a centrifugal pump. High-pressure forced lubrication by a submerged gear-type pump is applied to the principal bearings; other bearings are lubricated at lower pressure via a pressure-relief valve. An opposed twin-cyl 5-h.p. petrol engine is used for starting, and also for warming the main engine in cold weather. H. C. E.

823. 500 h.p. diesel-mechanical locomotive. Anon. *Gas Oil Pwr*, 1951, **46**, 348.—The main power unit is a Paxman 12RPH four-stroke engine with twelve cyl of dimensions 7 by 7¾ inches, rated at 500 b.h.p. at 1375 r.p.m. Water-cooling is provided, and a 24-V motor is used for starting.

The transmission is via a Vulcan-Sinclair coupling to a preselective six-speed and reverse gearbox. Details of the gearbox and frame construction are given.

The locomotive will haul up to 370 tons on grades of 1 in 48. Its weight in full working order is 55 tons, and the tractive effort in first gear is 35,400 lb. H. C. E.

824. Sleeve-valve diesel engine. H. R. Ricardo. *Gas Oil Pwr*, 1951, **46**, 309–12.—Describes early experiments with a sleeve-valve engine with cyl dimensions 5½-inch bore by 7-inch stroke. First designed as a petrol engine, it was found that, compared with a poppet-valve unit, the piston was cooler, with no trace of ring-sticking, and the mechanical efficiency was higher. Piston cooling is due to the action of the sleeve valve in distributing local concentrations of heat over the surface of the cyl. There is no convincing reason for the increased efficiency.

Experiments on air swirl in a high-speed diesel unit were made by inserting an anemometer into a motored engine and changing the angular setting of the swirl baffles. The results were expressed as swirl ratio = anemometer speed/crankshaft speed. Running the engine at fixed rate and constant fuel injection, it was found that max b.h.p. was obtained at an air-swirl ratio of *ca* 10; and fuel consumption of 0·34 lb/b.h.p.hr at a b.m.p. of 90 p.s.i. and piston speed 1500 ft/min was obtained.

The article concludes with a description of the Brotherhood–Ricardo sleeve-valve engine, which ranges from two to eight cyl of dimensions 7½-inch bore by 12-inch stroke, and operates at 900 r.p.m. to give an output of 50 h.p/cyl. H. C. E.

825. Governors and control gear for diesel engines. L. Berman. *Gas Oil Pwr*, 1951, **46**, 324.—A description is given of a centrifugal governor which uses a servo mechanism with lub. oil under pressure as the operating medium. Either the oil may be taken from the engine system or the governor may have its own oil tank and pump. The method of operation automatically provides that: (1) the engine cannot run until some oil pressure has been built up; (2) the fuel is cut off and the engine stops if the oil pressure falls below a predetermined value.

Oscillograph traces show that when full load is suddenly taken off an engine the governor begins to operate the fuel control after 0·2 sec, and fuel is reduced to the no-load value in 0·7 sec.

An isochronous governor, which maintains the engine at exactly constant speed when the load is altered, is also described. H. C. E.

826. Nordberg supairthermal diesel, duafuel and gas engines. R. Miller. *Gas Oil Pwr*, 1951, **46**, 283–5.—This theoretical paper presents an analysis of the effect of C.R., pressure, and temperature on engine output and efficiency. The application of the principles discussed is illustrated with reference to a Nordberg six-cylinder engine. (See also Abs. 324—1952.) H. C. E.

827. Modern gas engines. R. L. Boyer and W. R. Crooks. *Gas Oil Pwr*, 1951, **46**, 313–14, 318.—Describes the stages involved in converting diesel engines to operate on gas.

Early deficiencies in thermal efficiency were overcome by using a compression pressure of 450 p.s.i., which at an air/gas ratio of 17 : 1 acts as a 100-p.s.i. compression pressure at an air/gas ratio of 10 : 1. By varying the air/gas ratio the self-ignition point can be raised above the highest desirable compression pressure, and gas can therefore be used in turbo-charged four-cycle engines. It was also found possible to decrease the pilot diesel oil from 25 down to 4% of the total fuel, and finally to replace the diesel oil by an electric spark.

The latest design is the Cooper-Bessemer GMW engine. It is a two-stroke V unit with cyl of 18-inch bore and 20-inch stroke, and operates at 250 r.p.m. With from six to ten cyl, its max rating is 2500 b.h.p. H. C. E.

828. Design of the exhaust snubber for gas engines. R. L. Leadbetter. *Gas Oil Pwr*, 1951, **46**, 319.—When the first chamber of a snubber is a cyl of length $\geqslant$ dia, an ex-

plosion exerts its greatest force at a point near the end farthest from the engine. This effect is thought to arise because the momentum of the exploding gas in the backward end fails to overcome the inertia of the gas in the forward end. This idea is made the basis of the design of a snubber.

The value of explosion-relief devices is controversial, because the explosion cycle is probably complete before appreciable amounts of gas can escape through the relief opening. H. C. E.

829. Aero-engine oil systems for cold climates. A study of the problems of lubrication in arctic weather conditions. N. Sharp. *Airc. Engng*, 1951, **23** (274), 368–72.—After introductory remarks on the climatic conditions under which satisfactory operation is required, the objects of oil dilution are listed and the principle of operation of the conventional piston-engine oil-dilution system described. The reasons why the use of oil dilution is not detrimental to the engine are explained briefly, this being followed by a detailed consideration of the principal difficulty experienced with oil-dilution systems, namely poor segregation of the diluted oil contained in the hot pot from the undiluted oil in the main body of the tank. Tests are described which showed that faulty segregation cannot be attributed to diffusion at the make-up ports, whilst other factors (possible leakage of oil from the tank during standing, internal leakage in the tank between the undiluted and diluted oils, and inferior design of the internal details of the tank) which appeared to be possible causes of this segregation are also examined. Recommendations are made regarding points to be observed when designing oil tanks for use with oil dilution, the importance of proper shrouding of the make-up ports being stressed. The final section of the paper deals briefly with the problem of starting gas-turbine engines at low temp. In this case oil dilution is not practicable, and it is thought likely that, unless synthetic oils provide a satisfactory solution to this problem, considerable modification to the lubrication system may become necessary. N. L. A.

830. Compressed air starting system. Anon. *Gas Oil Pwr*, 1951, **46**, 340.—This unit comprises an engine-driven compressor, air-storage tank, distributor, and an injection valve on each cyl. Air at 550 p.s.i. is directed by the distributor to each of the valves in turn, thus operating the pistons in the correct sequence. H. C. E.

831. Improvements and modifications to the Farnboro engine indicator. R. W. S. Mitchell. *Gas Oil Pwr*, 1951, **46**, 272–4. **Recording pressure diagrams of internal combustion engines.** Anon. *Gas Oil Pwr*, 1951, **46**, 335–9, 347.—These articles discuss the routine measurement of peak cylinder pressures, compression pressures, etc. In the second article several methods are described and criticized. H. C. E.

Safety Precautions

832. Starving oil fires. G. Weber. *Oil Gas J.*, 20.12.51, **50** (33), 182.—Displacement of heated oil on surface of burning oil in tank is brought about rapidly and effectively by simple injection of air at low pressure at tank bottom, resulting in fire being reduced or snuffed.

In a full-scale test an open storage tank of burning kerosine was extinguished in 5 sec. G. A. C.

833. Automatic foam installation. K. Möbius and F. Emmrich. *World Petrol.*, 1952, **23** (1), 50–2.—(See Abs. 1557—1951.)

Miscellaneous

834. World production at all-time high. D. M. Duff. *Oil Gas J.*, 20.12.51, **50** (33), 229.—In spite of disappearance of Persia from ranks of major world producing areas, world output of crude oil rose to 11¾ million b.d., 12% higher than in 1950. Production in the U.S.A. increased by 13·7% and in Venezuela by 13·5%. G. A. C.

835. World demand to continue upward trend. A. D. Stewart. *Oil Gas J.*, 20.12.51, **50** (33), 270.—Tables show world-petroleum demand, world supply, and crude-oil-refining capacity, all excluding the U.S.S.R. and satellites. World demand for 1951 averaged 11 million b.d., an increase over last year of 9·2%. G. A. C.

836. The world's tank-ship fleet. B. Saurino. *Oil Gas J.*, 20.12.51, **50** (33), 280.—The analysis results in tables showing that tanker growth will match needs in 1954; bulk of new construction is outside the U.S.A.; post-war construction greatly exceeds pre-war; tankers on order; T–2 tanker flows of crude oil and products into major areas by origin, 1950; and relative utilization of world fleet for commercial petroleum trade 1950. G. A. C.

837. Shell to operate 30 per cent of total European refining capacity. Anon. *Oil Gas J.*, 20.12.51, **50** (33), 314.—A country-by-country analysis is given of progress during past five years in rehabilitating and modernizing manufacturing facilities. Countries include Belgium, France, Germany, Gt Britain, Italy, and the Netherlands. G. A. C.

838. Japan speeding refinery rehabilitation. Anon. *Oil Gas J.*, 20.12.51, **50** (33), 312.—Repair of war-damaged plant and modernization of other units in Japan is briefly reviewed. Nearly 90% of petroleum products needed in Japan are imported. G. A. C.

839. Oil refineries in 1951. Anon. *Engineer*, 1952, **193**, 74–6.—Review of U.K. developments. V. B.

840. Molecular distillation. H. Booy. *Ingenieur*, 22.12.51, **63**, Ch. 71.—The paper describes the principle of molecular distillation and points out the greatly reduced decomposition hazard as compared with normal distillation methods. A number of set-ups which give better than one plate separation are described, and sketches of the apparatuses concerned are included. The degassing of the feed material and the distillation rate are discussed in some detail. The application of the method for the distillation of temperature-sensitive materials and for the production of pure samples of Mg, Li, Na, Ca, and Hg is described at some length. R. R.

841. A steel plate thickness meter. S. S. Carlisle and B. O. Smith. *Engineer*, 1951, **192**, 805–8.—A non-destructive thickness tester for carbon and low-alloy steel plate is described, using a magnetic method. Measuring head of instrument consists of a pot-shaped electro-magnet with provision for indication of total magnetic flux in main magnet circuit. Measuring head is applied to plate to be tested producing saturation flux density in body of plate, total flux indicated being directly related to plate thickness. Range of instrument is 0 to 0·25 inches, with an accuracy of $\pm 0{\cdot}003$ inches or $\pm 3{\cdot}5\%$, whichever is greater. Reading is little affected by non-magnetic coatings (paint, rust, etc.) on steel surface. Deep pitting on plate surface has no appreciable effect on instrument's ability to measure thickness of residual sound metal. A. C.

842. Outside engineering firm to audit Bureau's synthetics cost data. Anon. *Petrol. Process.*, 1951, **6** (12), 1380–1.—As the result of a Bureau of Mines cost estimate for coal hydrogenation being considerably lower than that prepared by the National Petroleum Council, the firm of Ebasco Services Inc., New York, is to prepare an engineering audit and an independent evaluation of the cost of producing synthetic fuels from commercial-size hydrogenation plants. D. W. F.

843. Economic aspects of energy in the U.S.A. Ferrieu. *Bull. Ass. franç. Tech. Pétrole*, 1951 (90), 35–48.—Lecture. Reserves and transport of solid and liquid fuels are discussed. Fuel cost on thermal basis increases in order natural gas, bituminous coal, anthracite, crude oil, coke. Comparison is made between gas and electricity; between 1932 and 1949 natural gas and electricity sales both increased by a factor of about 4. Legislation and price tariffs covering these two energy sources are described. V. B.

844. Industrial boilers and power station boilers. P. Mercier. *Bull. Ass. franç. Tech. Pétrole*, 1951 (90), 7–23.—Lecture (illustrated) reviewing U.S. steam generation, which accounts for 70% of fuel consumption. Industrial plants inspected were mostly twenty to forty years old and mainly coal-fired. Evaporation rates were 12 to 65 kg/m²/hr, whilst pressures were generally 8 to 10 hpz. For boilers with capacity >15 ton steam/hr use of spreader stokers is increasing. In power-stations current practice is 500° C and 55 hpz pressure, 75% of power-station boilers (53% of total capacity) have hourly evaporation rates of <270 tons. About half power-stations use pulverized coal, the remainder either oil or gas or both. World's largest steam station has boiler operating at 570° C and 103 hpz with steam generation of 600 tons/hr. V. B.

845. I. M. Gubkin—founder of Soviet petroleum technology and geology. E. N. Shatzkii. *Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk*, 1951, 1854–60.—Appreciation on occasion of eightieth anniversary of birth of Gubkin (1871–1939). (Cf. Abs. 639—1950.) V. B.

846. History of the discovery of coal, petroleum and peat deposits in Russia. A. E. Probst. *Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk*, 1951, 1533–46.—A survey of finds reported in the seventeenth and early eighteenth centuries. V. B.

847. First and second year of Six Year Plan. Anon. *Nafta*, Jan. 1951, **7**, 1–2.—Statistical summary of progress in 1949 and 1950 and programme for 1951. M. S.

848. Geoanalytical researches in petroleum industry. L. Sulimirski *et al* (collected papers). *Proc. of Main Petroleum Institute*, (Polish) *Ministry of Mining*, Cracow, 1950. **No. 1**, pp. 37.—Seven short papers previously read before the [Polish] Petroleum Institute are presented in the form of a brochure. Their titles are " Geoanalytical Researches in Petroleum Industry," " Research into variations of surface tension of drilling mud and comparison with values obtained by Baroid apparatus," " Determination of helium in natural gases," " Baryties apparatus," " Research into radioactivity of rocks in petroleum drillholes," " Construction of cable connecting apparatus investigating radioactivity with the surface," " Interpretation of the results of the first electronic logging of a petroleum drillhole." Papers are illustrated by sketches and followed by discussion. M. S.

BOOK REVIEW

The nature of competition in gasoline distribution at the retail level. Ralph Cassady, Jr., and Wylie L. Jones. Berkeley and Los Angeles: University of California, 1951. Pp. xii + 220. $3.50.

The scope of this independent research project has been deliberately confined to one product, one marketing area of some 1000 million Imp. gal/annum, and one level of distribution. By this sort of micro-economic analysis of a factual competitive situation, the authors seek to confirm, vitiate, or refine some of the existing hypotheses in the theory of competition. The apparently parochial title should not be allowed to disguise the appeal to wider interests that this book has, as the very intensiveness of the survey brings to light many interesting facets of market behaviour, applicable to other and broader markets, which might be lost in a more extensive analysis. The 2½-year study period was one of particularly dynamic market conditions which ensures that price cutting, super stations, self-service, and other lively market phenomena come under the microscope.

The methodology is of interest as typifying the empirical testing of theory against fact, to the benefit of each, which is a feature of the close relationship between American universities and business interests, and which might with advantage be emulated to a greater extent in the U.K.

The authors start by examining the nature of the demand for motor spirit. Seasonal and cyclical variations, the price elasticity of demand, and factors underlying consumer behavour, such as choice of service station, are discussed. The operations of, and connexion between, the thirty-five major and independent wholesale suppliers and the 6800 retail outlets in the market are then examined. A substantial degree of forward integration is noted, generally stopping short of the retail level, although suppliers have a considerable measure of indirect control of retail policies. The existence of sources of supply other than major companies is found to have an important effect on the competitive situation and price structure, particularly as there is stated to be little significant difference in the qualities of the products offered by various suppliers. Important operational differences between major and independent suppliers are detected in such matters as distribution methods, degree of control over outlets, maintenance of retail prices, price competition, and credit cards.

Turning to competitive behaviour, the authors distinguish three main groups—"conservative," "aggressive," and "defensive" competitors. Conservative competitors, normally 75 per cent of total outlets, are mostly dealers for, and considerably influenced by, major companies. Competition by this group is marked by emphasis on quality of the product-service, as opposed to price cutting, as any price reduction in a major company's product by one dealer invariably spreads to overlapping sub-markets until it has been generalized, with no net advantage because of the inelastic response of total motor spirit sales. Aggressive competitors, on the other hand, are liable to gain very considerably from price cutting. This action on their part need not inevitably result in retaliation by majors who may be reluctant to endanger general price stability. Consequently, as the demand for the product of one particular seller is likely to be highly elastic, a large increase in volume may reward the price cut. This group, generally deciding their own policies and often promoting their own brands, is found to play a price-depressant role more important than their normal 15 to 20 per cent of the trade suggests. It is of interest to note that a large proportion of their supplies originates with majors, which is held as evidence of active competition at wholesale. Defensive price cutting is normally employed as a compensatory device by dealers operating under some disadvantage, such as a little-known brand or a bad site, in order to keep in the market. In abnormal circumstances, however, a large shift may occur from the conservative to the defensive category, as happened increasingly in the area

covered by this study after mid-1949, when major companies' dealers were forced by aggressive competition to adopt defensive price cuts.

Turning to dealer margins, the authors give an account both of the differences between wholesale and retail prices and also the adjustments which may be negotiated between supplier and dealer by manipulation of the rental allowance. Variations in margins over time and between localities and dealers are reviewed.

The determination of retail prices in the area is then examined in the light of these various forms of competition, product quality, wholesale and crude prices. Prior to the 1950 price war, close uniformity of prices is found to have been typical among major company dealers with Standard Oil of California the market leader, although " under the canopy " concessions to favoured patrons were common in non-company operated stations. Most independent company stations at this time operated 2 to 3 cents a gallon below the major's level, while aggressive price cutters, especially self-serves, offered reductions on a major brand price of up to 5 cents, although this was on a limited scale. By mid-1950, price cutting and promotional price signs are shown to be almost universal, due largely to the aggressive action of volume outlets, with the differential between major company dealers and volume outlets reduced to a little over 2 cents.

In general, the authors conclude from their analysis that there is sharp competition within the study area which increased in intensity in the period under review and also changed in emphasis from non-price to price rivalry. This increase in tempo was due, on the demand side, to increased consumer responsiveness to price competition and, on the supply side, to stock surpluses coming on the market through independent suppliers and an increasing number of outlets, particularly of the aggressive type. These mass distributors are thought to have had a considerable influence on policies other than price, such as the size, layout, location, and storage facilities of sites, but, in general, the authors feel that there is room for both conventional outlets and volume distributors, with or without service, to cater for those consumers who are price conscious.

One point of criticism is the large number of footnotes which tend either to distract attention from the main argument in the narrative or to be ignored, which in many cases would be a pity. There is no index and, although its provision would doubtless be difficult in a work of this nature, its absence detracts from the value of this book for reference purposes. C. P. D.

ADDITIONS TO THE LIBRARY

Akademiya Nauk S.S.S.R. Trudui paleontologicheskogo instituta. (Academy of Sciences of the U.S.S.R. Proceedings of the Paleontological Institute).

Vol. XXIV. (1950). **Tafonomiya i geologicheskaya letopsis'** (Taphonomy and geological chronicles). **1. Zakhoronenie nazemnuikh faun v paleozoe** (Burial of surface fauna in the paleozoic). 178 pp. I. A. Efremov.

Vol. XXV. (1950). **Rod *Palaeogadus* i ego razvitie.** (The genus *Palaeogadus* and its development). Pp. 1–25. P. G. Danil'chenko.

Rod *Centriscus* iz maikopskikh otlozhenii kavkasa. (The genus *Centriscus* from the Maikop deposits of the Caucasus). Pp. 26–55. A. K. Rozhdestvenskii.

Vol. XXVI. (1950). **Rod *Triticites*, ego razvitie i stratigraficheskoe znachenie.** (The genus *Triticites*, its development and stratigraphical significance). 180 pp. S. E. Rozovskaya.

Vol. XXVII. (1950). ***Chonetidae* russkoi platformui.** (*Chonetidae* of the Russian plateau). 108 pp. A. N. Sokol'skaya.

Vol. XXVIII. (1950). **Plastinchatozhabernuie spirialisovuikh glin, ikh sreda i zhizn'.** (Lamellibranchia of Spirialisov clays, their medium and life). 99 pp. R. L. Merklin.

Vol. XXIX. (1950). **Verkhnekamennougol'nuie ammonitui urala.** (Upper carboniferous ammonites of the Urals). 223 pp. V. E. Ruzhentzev.

Vol. XXXIV. (1951). **Pozdnedevonskie korallui *Rugosa*, ikh sistematika i evolyurziya.** (Late-Devonian corals *Rugosa*, their systematism and evolution. 121 pp. E. D. Soshkina.

British Standards Institution : London.

BS 46 : Part 3 : 1951. Solid and Split Taper Pins. Pp. 13. 2*s*. 6*d*. net, post free.

BS 1813 : 1951. Dimensions of Conduit Dies. Pp. 12. 2*s*. net, post free.

BS 1812 : 1951. Textile Screening Cloths. Pp. 17. 2*s*. net, post free.

BS 394 : 1951. Short Link Wrought Iron Chain (excluding pitched or calibrated chain). Pp. 14. 2*s*. net, post free.

BS 978 : 1952. Gears for Instruments and Clockwork Mechanisms; Part 2, Cycloidal Type Gears. Pp. 12. 3*s*. 6*d*. net, post free. Part 3, Bevel Gears. Pp. 8. 3*s*. 6*d*. net, post free.

BS 1132 : 1952. Automatic Pipettes : Pp. 9. 2*s*. net, post free.

BS 1696 : 1951. Short Link Wrought Iron Chain of Special Quality (excluding pitched or calibrated chain). Pp. 14. 2*s*. net, post free.

BS 1806 : 1951. Dimensions of Toroidal Sealing Rings. Pp. 16. 2*s*. 6*d*. net, post free.

BS 1814 : 1952. Marking System for Grinding Wheels. Pp. 7. 2*s*. net, post free.

Progress in Petroleum Technology. Washington, D.C. : American Chemical Society, 1951. Pp. 392 + vi.

In September 1951 the Division of Petroleum Chemistry of the ACS presented at the Diamond Jubilee meeting in New York a symposium on twenty-five years' progress in petroleum technology. The thirty-two papers so presented constitute the contents of this book, and the authors of the individual papers are all well-known in the industry.

The emphasis is on the chemical side of the petroleum industry, with particular reference to the various processes and their development over the last quarter of a century.

In the opening paper Dr Robert E. Wilson picks out the highlights of the period under review and concludes that the next twenty-five years will see a still greater broadening of the scope of petroleum research.

Vacuum Physics. London: The Institute of Physics, 1951. Pp. 80 + iv. 15*s*.

In June 1950 the Midland Branch of the Institute of Physics held a symposium on the subject of vacuum physics and its applications in science and industry. Eleven papers were read and discussed and dealt with such matters as vacuum pumps, systems, and gauges, with leak detection, and the use of vacuum in dehydration, coating plant, melting and sintering of metals, freeze drying, etc.

Oil Shale and Cannel Coal. Vol. 2. Ed. George Sell. London: Institute of Petroleum, 1951. Pp. xx + 832. 63*s*. post free.

Proceedings of the Second Oil Shale and Cannel Coal Conference, organized by the Institute of Petroleum and held in Glasgow in July 1950.

THE INSTITUTE OF PETROLEUM

NOTICES, MARCH 1952

ENTRANCE FEES AND SUBSCRIPTIONS

The current Entrance Fees and Annual Subscriptions for membership of the Institute are :

	Entrance Fee	*Annual Subscription*
	£ *s.* *d.*	£ *s.* *d.*
Members and Fellows	2 2 0	4 4 0
Associate Members and Associate Fellows .	1 1 0	3 3 0
Student Members	Nil	1 1 0

APPLICATIONS FOR MEMBERSHIP OR TRANSFER

The following have applied for admission to or transfer of membership in the Institute. In accordance with the By-laws, the proposals will not be considered until the lapse of at least one month after the publication of this *Journal*, during which time any Fellow, Member, Associate Fellow, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of the candidate.

The object of this information is to assist the Council in grading the candidate according to the class of membership.

The name of candidates' proposers and seconders are given in parentheses.

Application for Membership

BALMER, Leslie Claud, stores foreman, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

BEAKE, Robert Clayton, executive engineer, Regent Oil Co. Ltd. (*C. Sefton*; *E. P. Wright.*)

BIRD, Eric Albert, works chemist, Thames Tar Products & Contractors Ltd.

BLACKBURN, Sydney Dennis, Captain, R.A.S.C. (*R. F. Sanderson*; *W. H. Kelly.*)

BLAKENEY, Robert Clifford, stores foreman, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

BOLAND, Brian Jerome, student apprentice, National Oil Refineries Ltd. (*P. F. Ellis*; *E. J. Horley.*)

BREW, William Raymond Thomas, stores supervisor, Kuwait Oil Co. Ltd. (*E. Boaden*; *W. C. Buie.*)

BURGESS, William Norman, storekeeper, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

CARSWELL, John R., assistant stores superintendent, Gulf Oil Corporation. (*D. S. Curtis*; *E. Boaden.*)

CARSWELL, Ronald Alec, storekeeper, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

CLARKE, William David, assistant superintendent of research and development, Bahrein Petroleum Company. (*N. E. Watson*; *L. H. T. Walker.*)

COOK, Stanley Charles, technical sales superintendent, Messrs. LeGrand Sutcliff & Gell Ltd. (*C. J. Johnson*; *W. Rutherford.*)

D'ARCY, Hugh, chief storekeeper, Kuwait Oil Co. Ltd. (*R. M. S. Owen*; *E. Boaden.*)

DUNN, Gordon, draughtsman, Anglo-Iranian Oil Co. Ltd.

EARLL, Michael John, instrument engineer, Anglo-Iranian Oil Co. Ltd. (*E. J. Horley*; *G. Davies.*)

FENTON, John Anthony Lawrence, general trainee, Regent Oil Co. Ltd. (*T. E. A. Benjamin*; *J. R. Taylor.*)

GERRARD, John Stephenson, corrosion engineer, Kuwait Oil Co. Ltd. (*E. Boaden*; *W. C. Buie.*)

GIBSON, John David Edward, student apprentice, National Oil Refineries Ltd. (*E. J. Horley*; *G. Davies.*)

GORDON, Anthony Douglas, storekeeper, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

HAMES, Dion Christopher, student apprentice, National Oil Refineries Ltd. (*P. F. Ellis*; *E. J. Horley.*)

HATCHER, Stanley Ronald, student, Birmingham University. (*F. H. Garner*; *G. Sell.*)

HAYWARD, Russell Dallas, assistant works manager, Messrs. Berry Wiggins & Co. Ltd. (*F. H. Sanderson*; *F. W. Martin.*)

HUTTON, Edward Arthur, assistant to cargo superintendent, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

JEFFERY, Arthur Watson, instructor, National Oil Refineries Ltd. (*P. F. Ellis*; *E. J. Horley.*)

KEMPSON, John Stuart, storekeeper, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

LACEY, John Robert, student, Royal School of Mines. (*S. E. Coomber*; *G. D. Hobson.*)

LENNY, Leslie Mark, assistant operator, National Oil Pty. Ltd. (*G. E. Mapstone*; *G. Sell.*)

LEONARD, Joseph Ronald, R.A.F. Equipment Officer, Royal Air Force. (*C. Hartnell-Parker.*)

MCCLUNE, Gordon, chemical engineer, Nordac Ltd. (*A. Davies*; *V. F. T. Smith.*)

MARTIN, Ivan Ronald, stores foreman, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

MASON, Frank Anthony, student apprentice, National Oil Refineries Ltd. (*E. J. Horley*; *G. Davies.*)

MATTHEWS, Albert Edward, storekeeper, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

MIDDLETON, Cecil, stores foreman, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

MINAHAN, Neville John, storekeeper, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

NOTTES, Ernest, refinery superintendent and chief chemist, National Oil Pty. Ltd. (*G. E. Mapstone*; *G. Sell.*)

PARKER, Eric Ronald, cargo storekeeper, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *R. E. Martin.*)

PHILLIPS, John Best, chemical engineer, National Oil Refineries Ltd. (*E. J. Horley*; *G. Davies.*)

PHILLIPS, William Alexander, area manager and technical advisor, Falcon Oil Co. Ltd. (*E. Cunnah*; *R. Macdonald.*)

POLLEY, William Henry, assistant to stores superintendent, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

PRICE, George Frederick, stores foreman, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

PRYOR, Ian Reginald, assistant operator, National Oil Pty. Ltd. (*G. E. Mapstone*; *G. Sell.*)

RYNER, Thomas George, stores supervisor, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

RICHARDSON, William Henry Langdon, cargo superintendent, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

RUSSELL, Harold George, superintendent of research and development, Bahrein Petroleum Co. (*N. E. Watson*; *L. H. T. Walker.*)

RYAN, Arthur Norman, technical officer, Shell Co. of Australia Ltd. (*R. H. Street*; *R. B. Baillie.*)

SANDERS-HEWETT, Guy Scott, assistant works manager, Intrade Ltd. (*E. D. Lindop.*)

SMITH, Adam Reid, storekeeper, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

SPIKINS, William Charles, storekeeper, Kuwait Oil Co. Ltd. (*D. S. Curtis*; *E. Boaden.*)

STEEL, Howard James, sales representative, Shell-Mex & B.P. Ltd.

THOMAS, Stanley Richmond, student apprentice, National Oil Refineries Ltd. (*E. J. Horley*; *G. Davies.*)

TURK, Anthony John, engineering trainee, Anglo-Iranian Oil Co. Ltd. (*P. F. Ellis*; *E. J. Horley.*)

TRIMM, Geoffrey Alan, student apprentice, National Oil Refineries Ltd. (*E. J. Horley*; *G. Davies.*)

WHITELEY, Jack Leonard, station superintendent, Anglo-Iranian Oil Co. Ltd. (*B. D. Cauthrey*; *K. B. Ross.*)

WILDE, John Willatts, student apprentice, National Oil Refineries Ltd. (*P. F. Ellis*; *E. J. Horley.*)

WILLIAMS, Tegwyn, student apprentice, National Oil Refineries Ltd. (*E. J. Horley*; *G. Davies.*)

WILLIAMSON, Colin Potter, development section head, Anglo-Iranian Oil Co. Ltd. (*A. R. Stark*; *W. H. Thomas.*)

WILSON, Reginald Lawrence, assistant works chemist, Messrs. Berry Wiggins & Co. Ltd. (*G. W. D. Holmes*; *J. M. Nuttall.*)

Transfers

BADDELEY, Denis Irvine, petroleum technologist, Anglo-Iranian Oil Co. Ltd. (*F. Gill*; *R. F. Sanderson*) (*Associate Member to Associate Fellow.*)

FRITH, John Frederick Spencer, lecturer in chemical engineering, University of Sydney. (*F. H. Garner*; *I. G. Hunter*) (*Student to Associate Fellow.*)

JOHNSON, Horace, chemical engineer, Messrs. W. W. Hill, Son & Wallace Ltd. (*G. M. Davies*; *G. Sell*) (*Associate Fellow to Member or Fellow.*)

NEW MEMBERS

The following elections have been made by the Council in accordance with the By-laws.

Elections are subject to confirmation in accordance with the By-laws.

As Fellows

FROST, J. K. POLLOCK, M.

Transferred from Associate Member to Fellow

WILSON, A.

As Associate Fellows

BLANNER, A.	FROST, E.	LAURIE, R. A.
COTTER, W. H.	HALL, C. S.	LEAVETT, B. C.
DE MESTRE, R. E.	HARRISS, D. S. M.	LOCK, J. L.
EVERETT, E. G.	HETHERINGTON, J. A.	SMITH, R. K.

Transferred from Associate Member to Associate Fellow

CHIR, V. J.

Transferred from Students to Associate Fellows

COWAN, H.	MALPAS, W. E.
CRAWFORD, E. R.	OWENS, R. E.
EVANS, H. S.	SMITH, J. K.
HIBBERT, E. D.	WILSON, B. S.

As Associate Members

BAKER, R. J.	FOSKETT, C. W.
BUSHE, P. D. S.	HOLTER, J. E.

As Students

ABOLFATHI, Y.	KILPATRICK, J.
HAINES, P. A. T.	WRIGHT, J. T. M.

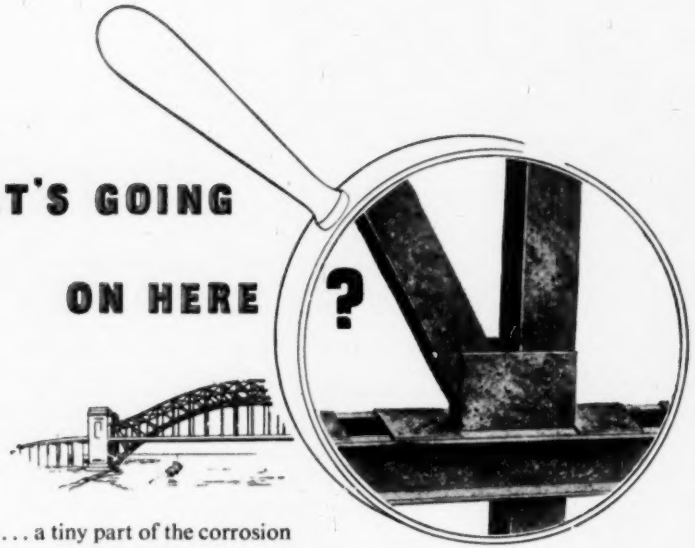
As Member-Company

JOHN THOMPSON LTD

As Collective-Member

NATIONAL COAL BOARD (SCOTTISH DIV'N. FIFESHIRE)

WHAT'S GOING ON HERE ?



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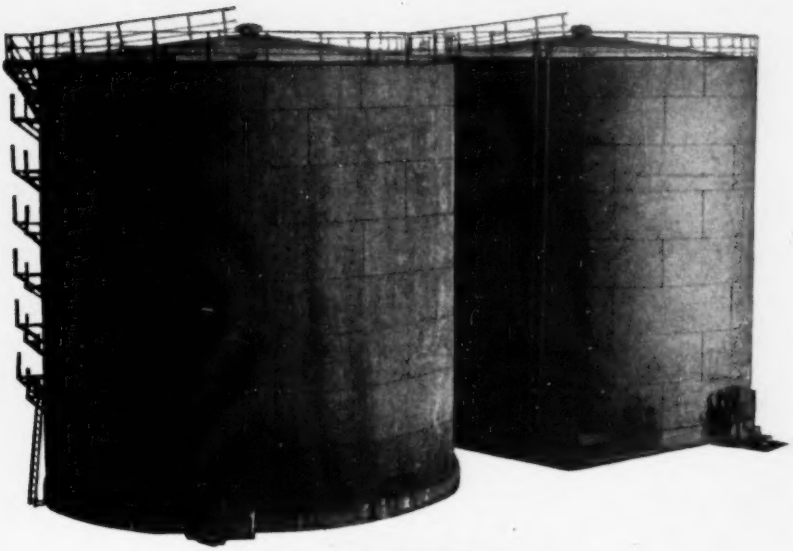

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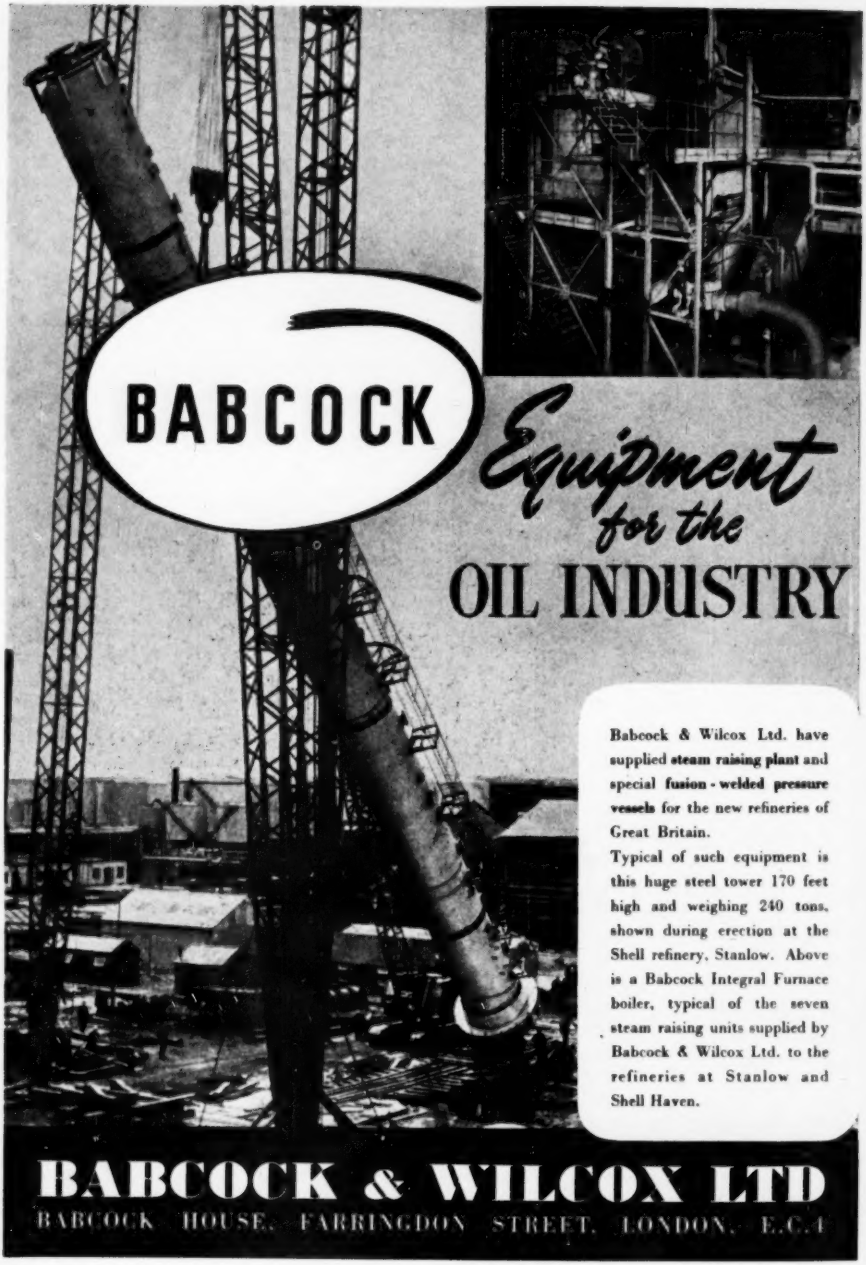
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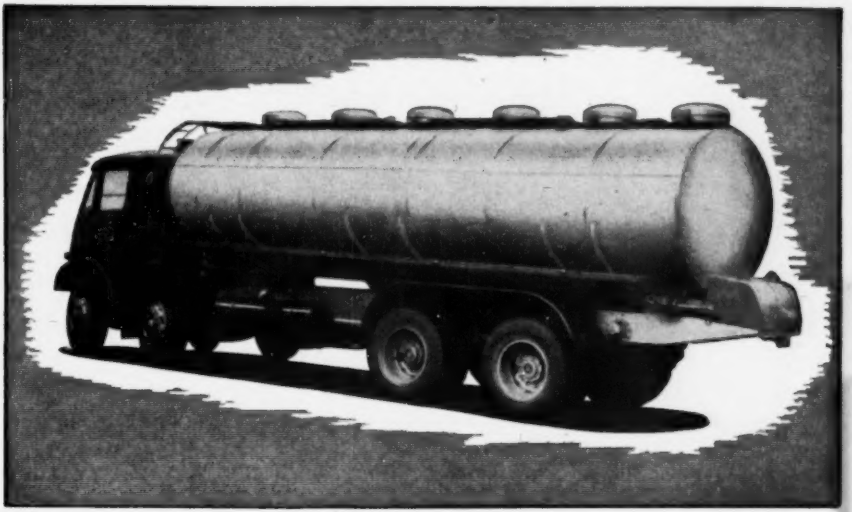

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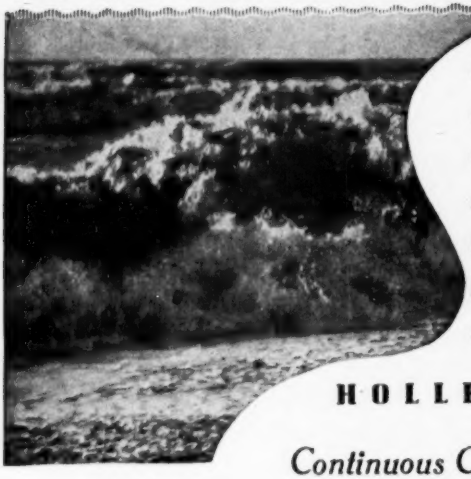

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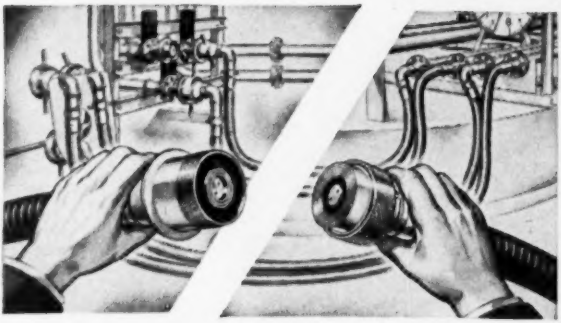

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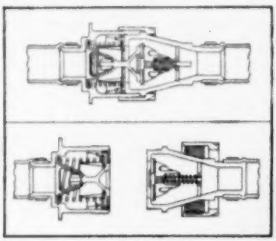

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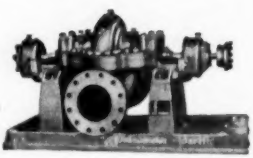

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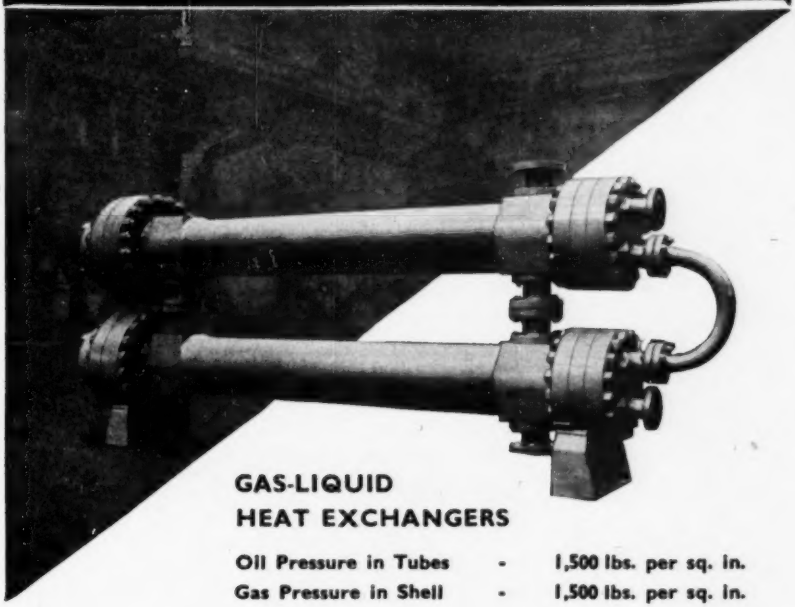

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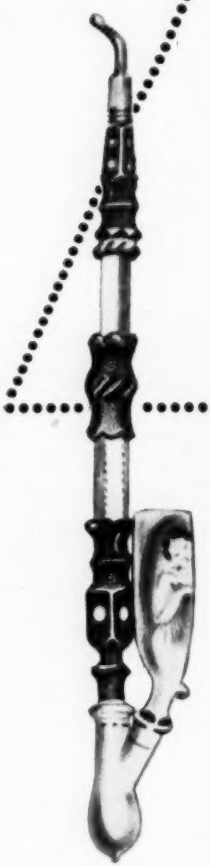
NUMBER SEVEN

TALKING OF PIPES



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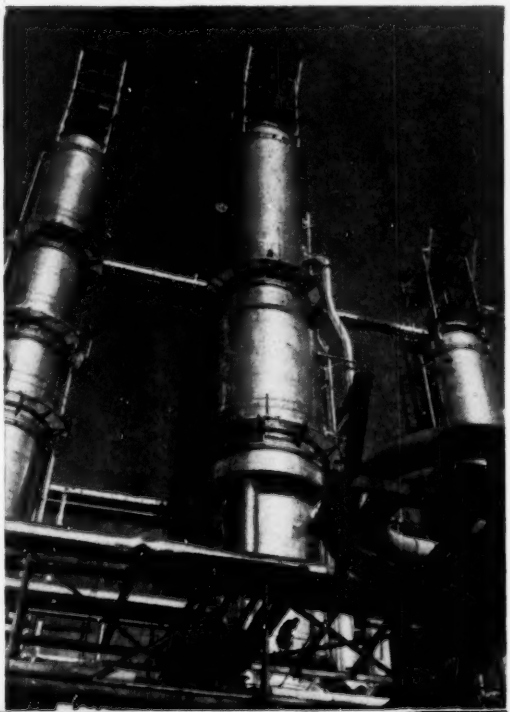

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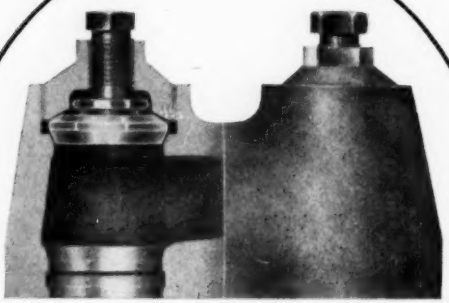

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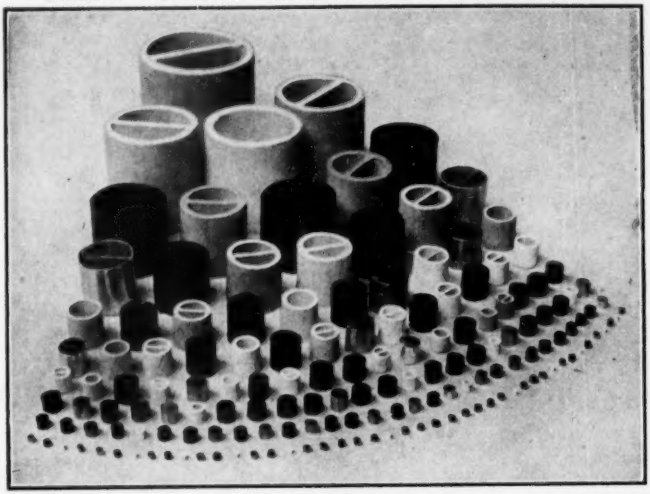

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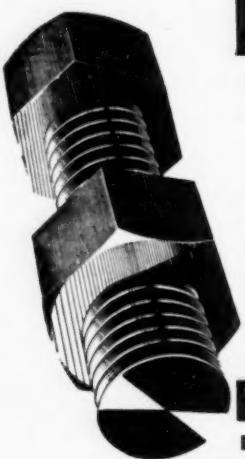

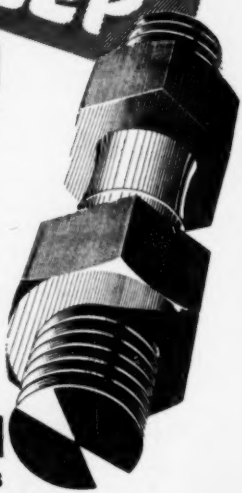

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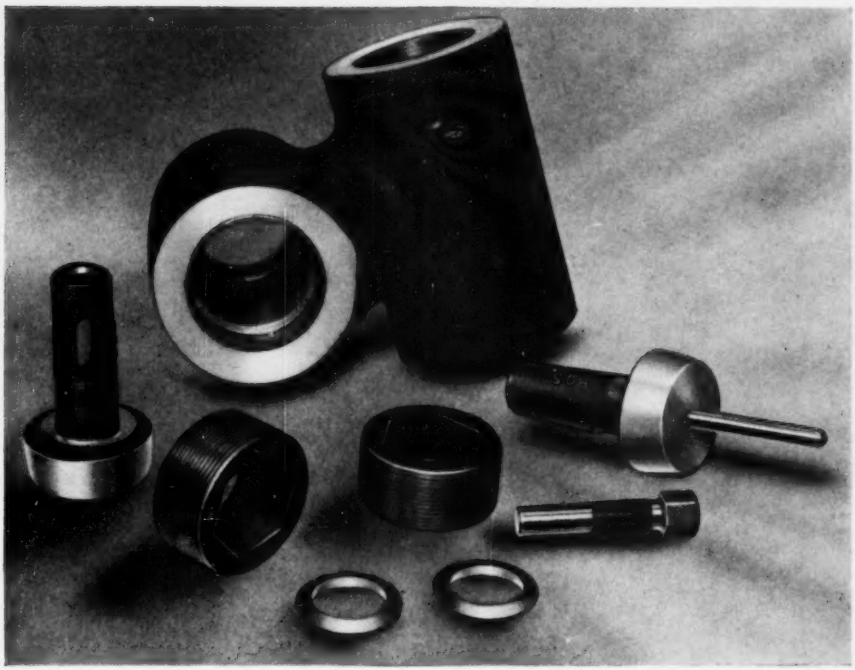

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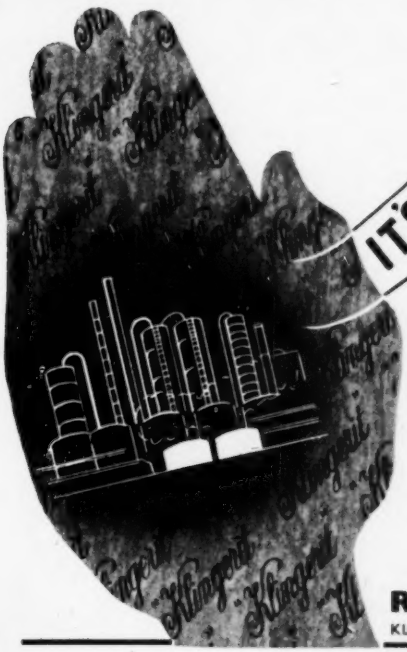

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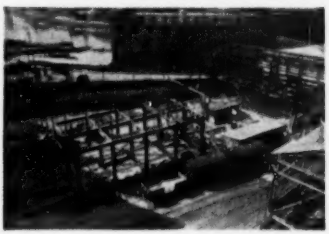
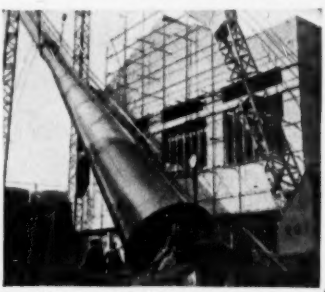


Erection of Silo Steelwork, foundations for storage tanks and construction of oil fuel tanks



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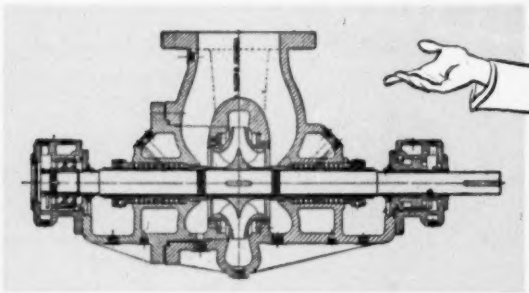

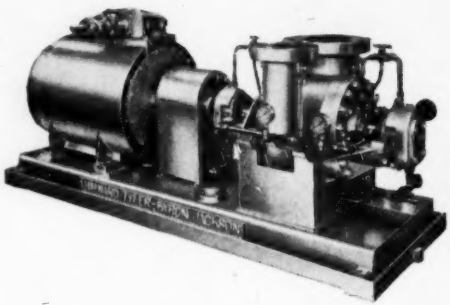

Illustration shows Hayward Tyler-Byron Jackson 6 x 8 x 10 Double Suction - Single Stage Refinery Pump, Type— D.S.H.O.

Just examine a few of the features of this standard pump from the Hayward Tyler-Byron Jackson range of Refinery Pumps, and it is easy to understand why they enjoy their high world wide reputation. Double Entry Impellers with unusually large fluid passages are fitted to give high duty at high speed, excellent suction and minimum reduction of performance with viscous fluids. Vertical split case with fully trapped armoured ring joints easy to make and remake to hold high pressure. Complete dismantling of the pump is possible without disturbing piping, driver, pump case or alignment of set.

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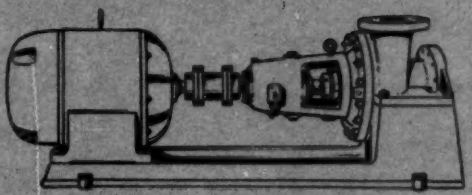
CENTRIFUGALS -

Type E.S. Single-Stage Process Pumps



These single-suction pumps are designed with vertically-split case for services where (1) continuous operation is important, (2) temperatures or pressures may be very high, (3) hot or cold liquids are handled near their boiling points and (4) broad capacity range at high efficiency is desirable.
Their design permits maximum interchangeability of parts. Only 3 sizes of bearing brackets, sleeves, packings, shafts and bearings are required for 18 pump sizes; which provide capacity ranges from 40 to 1500 gpm, differential heads from 40 to 1000 feet, speed ranges from 1750 to 4000 rpm, horsepower ranges from 2 to 250, with permissable temperatures up to 900°F.

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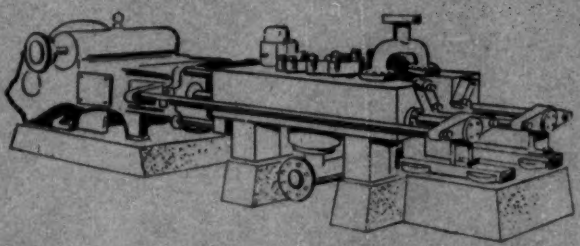

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